ANALYTICA CHIMICA ACTA

Vol. 10 (1954)

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THE MOLECULAR AND IONIC SOLUBILITY OF NICKEL DIMETHYLGLYOXIMATE

by

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Both from the theoretical and practical standpoints it is desirable to have fairly exact values for the molecular solubilities, the solubility product constants and the ionization constants of slightly soluble metal-chelate complexes. The present paper supplies these constants for nickel dimethylglyoximate and for dimethylglyoxime.

Writing dimethylglyoxime as $\mathrm{H_2Dx}$, we have the following expressions for the constants mentioned at constant ionic strength:

$$\frac{a\mathrm{H}^+[\mathrm{HDx}^-]}{[\mathrm{H_2Dx}]} = K'_{\mathrm{H_2Dx}}$$

(primary ionization constant of dimethylglyoxime; the prime denotes the mixed activity-concentration constant)

$$a\mathrm{H}^+[\mathrm{HDx}^-] = K'_{\mathrm{H_2Dx}}[\mathrm{H_2Dx}]_{\mathrm{sat.}}$$

($[\mathrm{H_2Dx}]_{\mathrm{sat.}}$ = molar solubility of $\mathrm{H_2Dx}$)

$$= L'_{\mathrm{H_2Dx}}$$

(solubility product constant of $\mathrm{H_2Dx}$)

$$\frac{[\mathrm{Ni}^{+2}]\,[\mathrm{HDx}^-]^2}{[\mathrm{Ni(HDx)_2}]} = K'_{\mathrm{Ni(HDx)_2}}$$

(ionization constant of nickel dimethylglyoximate)

$$[\mathrm{Ni}^{+2}]\,[\mathrm{HDx}^-]^2 = K'_{\mathrm{Ni(HDx)_2}}[\mathrm{Ni(HDx)_2}]_{\mathrm{sat.}} = L'_{\mathrm{Ni(HDx)_2}}$$

$K'_{\mathrm{H_2Dx}}$ has been obtained from the solubility of dimethylglyoxime in basic solutions combined with its molecular solubility, $L'_{\mathrm{Ni(HDx)_2}}$ from the solubility of nickel dimethylglyoximate in acidic solutions, and $[\mathrm{Ni(HDx)_2}]_{\mathrm{sat.}}$ (and therewith $K'_{\mathrm{Ni(HDx)_2}}$) from its solubility in slightly acidic or basic solutions saturated with dimethylglyoxime to reduce the ionic solubility to a negligible amount.

EXPERIMENTAL

The solubility of dimethylglyoxime was obtained by mechanically shaking sublimed crystals with water or aqueous solution for several hours to attainment of equilibrium and determining dimethylglyoxime in the filtered solution by hydrolyzing to hydroxylamine by boiling with hydrochloric acid, oxidizing hydroxylamine with excess potassium bromate, and titrating the excess iodometrically. The method for the determination of dimethylglyoxime was studied in some detail and a procedure was developed which gave a precision of ± 0.5%.

For the determination of the solubility of dimethylglyoxime in basic solutions, sodium carbonate-bicarbonate buffers or sodium hydroxide solutions were used; the ionic strength was maintained at $0.050M$ with sodium chloride. A few determinations (yielding anomalous results) were made in borate buffers. The pH was measured with a Beckman pH meter (type G) with an alkaline glass electrode.

The molecular solubility of nickel dimethylglyoximate in aqueous solutions was found by shaking the solution for 6 hours or more with an excess of solid nickel dimethylglyoximate and dimethylglyoxime, and determining nickel in 75 to 200 ml of filtrate by extracting with two 5 ml portions of chloroform and measuring the optical density of the latter at 375 mμ. The colored species (yellow) in the chloroform is nickel dimethylglyoximate. As a check on this determination, the chloroform extract was shaken with $0.2M$ hydrochloric acid to transfer nickel to the aqueous phase, in which it then was determined by a modification of ROLLET's colorimetric method, with bromine as the oxidizing agent.

In the determination of the solubility product constant of nickel dimethylglyoximate, an excess of the solid was shaken with hydrochloric acid-potassium chloride mixtures having a constant ionic strength of $0.050M$. Two nickel dimethylglyoximate preparations were used, one obtained by precipitation with excess dimethylglyoxime, the other with excess nickel, both at 100°; they gave identical results. The solid was stored in the moist state; equilibrium was reached more slowly with dried material. In most of the solubility determinations an excess of dimethylglyoxime was also present. The slow hydrolysis of dimethylglyoxime which occurs in acid solution is then of no significance. The saturated solutions were filtered through sintered glass and nickel was determined spectrophotometrically by ROLLET's method in the filtrate.

The solubility of nickel dimethylglyoximate was also determined in solutions buffered with biphthalate, but complexing of nickel ion takes place in such a medium, and the results are not reported here.

RESULTS AND DISCUSSION

Table I gives the solubility of dimethylglyoxime in water and sodium chloride solutions. The values reported are averages of a number of closely agreeing replicate determinations. Because of its very weak acidic properties, dimethylglyoxime exists almost entirely in the molecular form in these solutions. Its solubility is decreased by electrolytes because of the salting out effect. The data for sodium chloride solutions follow the SETCHENOW equation

$$\log f = k\mu,$$

where f is the activity coefficient of dimethylglyoxime (ratio of solubility in water to solubility in the electrolyte solution), k is a constant, and μ is the ionic strength. For sodium chloride, k is found to have the value 0.19.

The solubility of dimethylglyoxime in basic solutions as a function of $1/a\text{H}^+$ is graphed in Fig. 1. In sodium carbonate-bicarbonate buffers or in sodium hydroxide solutions a linear relation is obtained in accordance with expectations. Up to a pH of at least 11 the secondary ionization of dimethylglyoxime does not play a significant role. The abnormally high solubility found in borate buffers is doubtless due to the formation of a weak complex between boric acid and dimethylglyoxime, involving the OH groups of the latter.

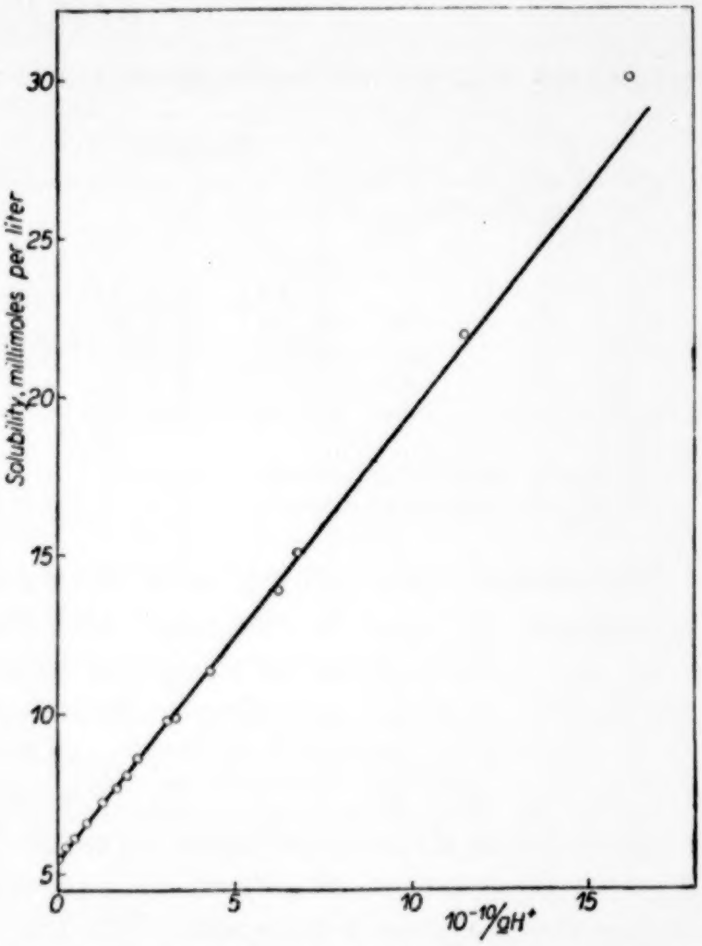

Fig. 1. Solubility of dimethylglyoxime as a function of $1/a\text{H}^+$.

The solubility of dimethylglyoxime in the pH range investigated is given by

$$S = [\text{H}_2\text{Dx}]_{\text{sat.}} + [\text{HDx}^-] = [\text{H}_2\text{Dx}]_{\text{sat.}} + \frac{K'_{\text{H}_2\text{Dx}}\,[\text{H}_2\text{Dx}]_{\text{sat.}}}{a\text{H}^+}$$

In Fig. 1, the intercept of the solubility line is equal to $[\text{H}_2\text{Dx}]_{\text{sat.}}$ and its slope is equal to $K'_{\text{H}_2\text{Dx}}[\text{H}_2\text{Dx}]_{\text{sat.}}$ The intercept has the value $5.43 \cdot 10^{-3} M$ (agreeing well with the value $5.37 \cdot 10^{-3} M$ in Table I), and the slope is $1.41 \cdot 10^{-13} M^2$, from which we obtain at ionic strength $0.05 M$:

$$K'_{\text{H}_2\text{Dx}} = 1.41 \cdot 10^{-13} / 5.4 \cdot 10^{-3} = 2.6 \cdot 10^{-11} \ (25^\circ).$$

If 0.86 is taken as the activity coefficient of HDx^- at $0.050 M$, the thermodynamic ionization constant is equal to

$$K_{\text{H}_2\text{D}} = \frac{0.86}{1.02} \cdot 2.6 \cdot 10^{-11} = 2.2 \cdot 10^{-11} \ (25^\circ)$$

where 1.02 is the activity coefficient of Ni(HDx)_2 at $0.05 M$.

References p. 9

TABLE I

SOLUBILITY OF DIMETHYLGLYOXIME IN WATER AND SODIUM CHLORIDE SOLUTIONS (25°)

Medium		Solubility	
		$\cdot 10^3 M$	
H_2O		5.43*	5.52**
NaCl,	0.05M	5.36*	5.38**
NaCl,	0.5M	4.44	
NaCl,	5.0M	0.61	

* From undersaturation
** From supersaturation

The present value of 0.632 g per liter for the solubility of dimethylglyoxime in water at 25° may be compared with the following earlier values:

0.74 g/l by interpolation from data of PONZIO[1]
0.30 g/l according to STROMBERG AND ZELYANSKAYA[2]
0.50 g/l ,, ,, BABKO AND MIKHELSON[3]
0.53 g/l ,, ,, STROMBERG[4]

BABKO AND MIKHELSON[3] have reported $8 \cdot 10^{-12}$ for the ionization constant of dimethylglyoxime at 18°. From data reported by STROMBERG[4] on the solubility of dimethylglyoxime in ammonia, the value $2.3 \cdot 10^{-11}$ can be calculated for K'_{H_2Dx}.

From Table II it is seen that the molecular solubility of nickel dimethylglyoximate in water at an ionic strength of 0.05M corresponds to 57 ± 3 γ Ni per liter or $9.7 \cdot 10^{-7} M$. In water saturated with chloroform at the same ionic strength the solubility is a little larger, namely 69 γ Ni per liter or $1.2 \cdot 10^{-6}\ M$. In 2M sodium chloride the solubility is about half of that in 0.05M solution. Proof that the solubility values obtained are actually those of molecular nickel dimethylglyoximate and do not include a contribution from other species such as Ni^{+2}, $NiHDx^+$ and $NiOH^+$ is furnished by the constancy of the values found at varying pH.

PASSAMANECK[5] states that the solubility of nickel dimethylglyoximate in water is about 80 γ Ni per liter (temperature not specified). From a graph given by BARNICOAT[6], an approximate solubility value of 200 γ Ni per liter at room temperature may be derived.

The data obtained in the determination of the solubility of nickel dimethylglyoximate in acidic solutions at $\mu = 0.05M$ are tabulated in Table III and plotted in Fig. 2. Excluding No. 7b, the average value of the "mixed" solubility product constant L' based on measurements in solutions saturated with dimethylglyoxime is $4.3 \cdot 10^{-24}$. The activity solubility product constant, L, is equal to $4.3 \cdot 10^{-24}\ (0.57)\ (0.86)^2$ or $1.8 \cdot 10^{-24}$, where 0.57 and 0.86 are the activity coefficients of Ni^{+2} and HDx^- at 0.05M ionic strength, based on KIELLAND's[7] data for

TABLE II

MOLECULAR SOLUBILITY OF NICKEL DIMETHYLGLYOXIMATE IN AQUEOUS SOLUTIONS (25°)

Solution	pH	Solubility of $Ni(HDx)_2$ Micrograms Ni per liter A*	B**
0.05*M* CH_3COONH_4	6.7	54, 56	58, 55
0.05*M* CH_3COONH_4, 0.0006% Ni^{+2}***	6.6	56, 54	53, 53
0.05*M* CH_3COONa, $\sim$ 0.01*M* HCl	5.6	57, 60	59, 58
0.05*M* CH_3COONa, $\sim$ 0.01*M* HCl, 0.0006% Ni^{+2}***	5.6	58, 60	62, 59
0.05*M* $NaHCO_3$	8.9	—	57
0.05*M* $NaHCO_3$, 0.0006% Ni^{+2}***	8.9	57	54
0.05*M* $CH_3COONH_4 + CHCl_3$	6.7	65	71
0.05*M* CH_3COONa, $\sim$ 0.01*M* HCl + $CHCl_3$	5.6	72, 72	66, 65
0.05*M* NaCl + $CHCl_3$	7.0		72
2.0*M* NaCl	6.8	28, 27, 27	31, 30, 30

* From optical density of chloroform extract of $Ni(HDx)_2$.

** From photometric determination of Ni by ROLLET's method.

*** Equilibrium approached from supersaturation (nickel dimethylglyoximate formed in solution); in others equilibrium approached from undersaturation. All solutions saturated with H_2Dx.

TABLE III

SOLUBILITY OF NICKEL DIMETHYLGLYOXIMATE IN HCl-KCl AT 0.05*M* IONIC STRENGTH (25°)

No.	Time of shaking hrs	pH	$(aH^+)^2$	Total Ni concentration, $M \cdot 10^3$	$L' \cdot 10^{24}$
1a	10	2.155	$4.89 \cdot 10^{-5}$	10.34	4.2
1b	8	2.195	$4.07 \cdot 10^{-5}$	8.65	4.2
1c	6	2.235	$3.38 \cdot 10^{-5}$	7.41	4.3
1d	6	2.275	$2.83 \cdot 10^{-5}$	6.12	4.3
2a	8	2.295	$2.59 \cdot 10^{-5}$	5.95	4.5
2b	6	2.325	$2.25 \cdot 10^{-5}$	4.71	4.2
2c	6	2.46	$1.20 \cdot 10^{-5}$	2.72	4.5
3*	2.5	2.46	$1.20 \cdot 10^{-5}$	2.75	4.5
4a	6	2.495	$1.02 \cdot 10^{-5}$	2.45	4.8
4b	6	2.625	$5.61 \cdot 10^{-6}$	1.28	4.5
5a*	5	2.98	$1.10 \cdot 10^{-6}$	1.25	4.8
5b	6	2.77	$2.88 \cdot 10^{-6}$	0.65	4.4
6a	8	3.185	$4.26 \cdot 10^{-7}$	0.084	3.8
6b	5	3.38	$1.74 \cdot 10^{-7}$	0.034	3.8
6c	5	3.64	$5.25 \cdot 10^{-8}$	0.011	3.9
6d	10	3.64	$5.25 \cdot 10^{-8}$	0.013	4.5
7a*	9	5.28	$2.75 \cdot 10^{-11}$	0.038	5.0
7b	8	4.29	$2.63 \cdot 10^{-9}$	0.0017	5.1

* No dimethylglyoxime added; others saturated with dimethylglyoxime.

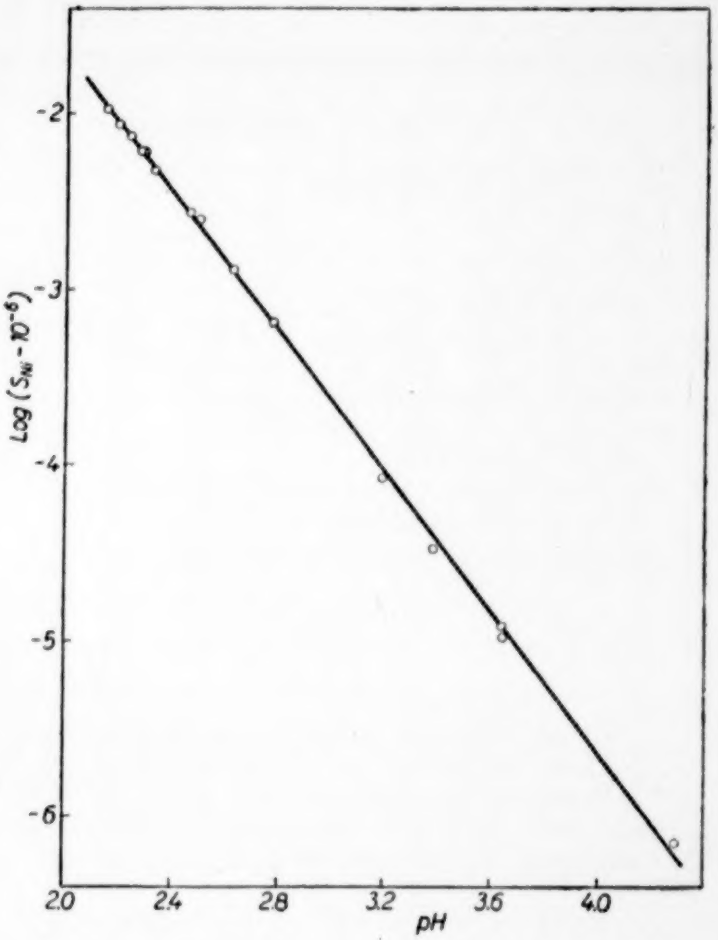

Fig. 2. Solubility of nickel dimethylglyoximate in acidic medium. (S_{Ni} = total molar concentration of nickel.)

individual ion activities. The constancy of the values of L' obtained at various pH's shows that no significant amount of an ion such as NiHDx^+ is present in the pH range 2 to 5. As already mentioned, the constancy of the values for the molecular solubility of nickel dimethylglyoximate (Table II) demonstrates the absence of appreciable amounts of NiHDx^+ at higher pH's. According to FREISER[8], nickel dimethylglyoximate in 50 per cent. dioxane solution ionizes in stages and he gives the values 10.46 and (9.9) for log K of the respective reactions $\text{Ni}^{+2} + \text{HDx}^- \rightleftarrows \text{NiHDx}^+$ and $\text{NiHDx}^+ + \text{HDx}^- \rightleftarrows \text{Ni(HDx)}_2$. Taking the molecular solubility of Ni(HDx)_2 as $9.7 \cdot 10^{-7} M$ (from Table II) we obtain the concentration and activity dissociation constants of nickel dimethylglyoximate:

$$K' = 4.3 \cdot 10^{-24} / 9.7 \cdot 10^{-7} = 4.4 \cdot 10^{-18} \ (\mu = 0.05)$$
$$K = 1.8 \cdot 10^{-24} / 9.7 \cdot 10^{-7} = 1.9 \cdot 10^{-18}$$

The extraction constant of nickel dimethylglyoximate

The present data permit calculation of the equilibrium constant for the extraction reaction:

$$\underset{\text{H}_2\text{O}}{\text{Ni}^{+2}} + \underset{\text{H}_2\text{O}}{2\text{H}_2\text{Dx}} \rightleftarrows \underset{\text{CHCl}_3}{\text{Ni(HDx)}_2} + \underset{\text{H}_2\text{O}}{2\text{H}^+}$$

$$K_{\text{ext.}} = \frac{[\text{Ni(HDx)}_2]_{\text{CHCl}_3} (a\text{H}^+)^2}{[\text{Ni}^{+2}] \, [\text{H}_2\text{Dx}]^2_{\text{H}_2\text{O}}}$$

(Since dimethylglyoxime is 12 times as soluble in water as in chloroform, it is convenient to base the equilibrium constant on the concentration of dimethylglyoxime in water instead of in the immiscible organic solvent, contrary to the practice in dealing with other metal-chelating reagents showing the opposite behavior.)

The value of $K_{\text{ext.}}$ is determined by the value of the partition coefficient of nickel dimethylglyoximate between chloroform and aqueous solution, and the values of the ionization constants, all at specified ionic strength:

$$K_{\text{ext.}} = \frac{\mathrm{P}_{\mathrm{Ni(HDx)_2}}\,(K'_{\mathrm{H_2Dx}})^2}{K'_{\mathrm{Ni(HDx)_2}}}$$

At 0.05M ionic strength and 25° we have:

$$K_{\text{ext.}} = \frac{(4.1\cdot10^{2}) \times (2.6\cdot10^{-11})^2}{4.4\cdot10^{-18}} = 0.063$$

(In the calculation of $P_{\mathrm{Ni(HDx)_2}}$, the solubility of $\mathrm{Ni(HDx)_2}$ in water saturated with chloroform has been used, *i.e.* $P_{\mathrm{Ni(HDx)_2}} = 28/0.069 = 4.1\cdot10^{2}$.)

The analyst is primarily interested in the *extraction coefficient*[9] of nickel:

$$E = \frac{\Sigma\,[\mathrm{Ni}]_{\mathrm{CHCl_3}}}{\Sigma\,[\mathrm{Ni}]_{\mathrm{H_2O}}} = \frac{[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}}{[\mathrm{Ni^{+2}}] + [\mathrm{Ni(HDx)_2}]_{\mathrm{H_2O}} + [\text{other forms of Ni}]}$$

In this expression, [other forms of Ni] refers primarily to soluble complexes or undissociated species that may be formed as the result of the presence of $\mathrm{NH_3}$, organic acids, etc., but includes $\mathrm{NiOH^+}$, $\mathrm{Ni(OH)_2}$, etc. Since the equilibrium concentration $[\mathrm{Ni(HDx)_2}]_{\mathrm{H_2O}}$ is approximately 1/400 of $[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}$, it is often much smaller than that of other forms of nickel in the water phase and can then be neglected. If, moreover, appreciable amounts of soluble nickel complexes are not present in the aqueous phase, we have the useful approximation:

$$\frac{\Sigma\,[\mathrm{Ni}]_{\mathrm{CHCl_3}}}{\Sigma\,[\mathrm{Ni}]_{\mathrm{H_2O}}} = \frac{[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}}{[\mathrm{Ni^{+2}}]_{\mathrm{H_2O}}} = K_{\text{ext.}}\,\frac{[\mathrm{H_2Dx}]^2_{\mathrm{H_2O}}}{(a\mathrm{H^+})^2}$$

On the other hand, when $[\mathrm{Ni(HDx)_2}]_{\mathrm{H_2O}}$ is large compared to other nickel species in the aqueous solution the extraction coefficient approaches the maximum value $\sim$ 400.

The value 0.063 calculated above for $K_{\text{ext.}}$ holds for 0.05M chloride medium, in which complexing of nickel appears to be small enough to neglect for analytical purposes.

The magnitude of $K_{\text{ext.}}$ is such that quantitative extraction of nickel can be obtained from weakly acidic medium. For example, at pH 5 with the aqueous solution saturated with dimethylglyoxime

$$\frac{[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}}{[\mathrm{Ni^{+2}}]_{\mathrm{H_2O}}} = \frac{0.063\ (5\cdot10^{-3})^2}{10^{-10}} = 1.6\cdot10^{4}$$

and the extraction coefficient will be determined by $[\mathrm{Ni(HDx)_2}]_{\mathrm{H_2O}}$ instead of $[\mathrm{Ni^{+2}}]$ and will equal $\sim$ 400. Nickel forms weak complexes with acetate ion, but from the dissociation constants of $\mathrm{NiAc_2}$ and $\mathrm{NiAc^+}$ given by FRONAEUS[10]

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it appears that the extraction of nickel can be made quantitative in 0.5*M* acetate medium at pH 5. Since dimethylglyoxime is much more soluble in water than in chloroform, it will usually be preferable to add it as an alcoholic solution, or possibly as an alkaline aqueous solution, instead of dissolving it in the chloroform.

TABLE IV

SOLUBILITY OF DIMETHYLGLYOXIME AND NICKEL DIMETHYLGLYOXIMATE IN CHLOROFORM (25°)

	Solubility	
	g/l	*M*
Dimethylglyoxime	0.052	$4.5 \cdot 10^{-4}$
Nickel dimethylglyoximate	0.141	$4.8 \cdot 10^{-4}$

The introduction of alcohol will change the value of $K_{ext.}$, but since the alcohol concentration in the aqueous solution need not exceed 5%, the change should not be great (*cf.* NUKA[11] on the effect of ethyl alcohol on the solubility of nickel dimethylglyoximate) and the above value can still be used for approximate calculations. If the volume of the chloroform phase does not exceed that of the aqueous solution, the concentration of dimethylglyoxime in the latter does not decrease much on successive extractions and the extraction coefficient of nickel dimethylglyoximate remains roughly constant.

In ammoniacal citrate medium, such as is used in separating traces of nickel from ferric iron and other metals, values of the constants for the complexing of nickel are required for the calculation of the extraction coefficient. It has been demonstrated experimentally that nickel can readily be extracted from such a medium[12].

Significance of molecular solubility of nickel dimethylglyoximate in precipitation

In analytical precipitations the solubility loss is generally assumed to be due to ionic solubility, as calculated from the solubility product constant, and the molecular solubility is neglected. From the figures given in Table II it is evident that for nickel dimethylglyoximate the ionic solubility can be reduced to such a minute value by the use of a relatively high concentration of HDx^- that the solubility loss will be determined by the molecular solubility. The latter is indeed very small, but still sufficiently large to require consideration in exact analysis. If the final volume in a precipitation of nickel dimethylglyoximate is 300 ml, the nickel remaining in solution in the molecular form is 0.017 mg, or ∼ 0.1 mg as nickel dimethylglyoximate, at 25°; if an alcoholic solution of dimethylglyoxime is used the molecular solubility will be greater. With a 1 g sample this molecular solubility loss corresponds to about 0.002% Ni, a figure of significance in highly accurate analyses (as of standard samples) when the nickel content is low.

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If the ionic solubility is considered negligible when it is 0.1 of the molecular solubility, a concentration of HDx^- equal to $\sqrt{10K'_{\mathrm{Ni(HDx)_2}}}$ or $\sim 7 \cdot 10^{-9}M$ (*e.g.* a solution of $0.05M$ ionic strength half saturated with H_2Dx at pH 5) should give the minimum useful solubility of the precipitate in the absence of complexing substances.

SUMMARY

Values are reported for the solubility product constant and the ionization constant of nickel(II) dimethylglyoximate in aqueous solution. The solubility of nickel dimethylglyoximate in the investigated pH range from 2 to 9 is accounted for by the species Ni^{+2} and $Ni(HDx)_2$; there is no evidence for the existence of a significant amount of $NiHDx^+$.

The extraction constant $\frac{[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}(a\mathrm{H^+})^2}{[\mathrm{Ni^{+2}}]\,[\mathrm{H_2Dx}]^2_{\mathrm{H_2O}}}$ has been calculated from the ionization constants of $Ni(HDx)_2$ and H_2Dx and the molecular solubilities of the former in water and chloroform.

RÉSUMÉ

Les valeurs du produit de solubilité et de la constante d'ionisation du diméthylglyoximate de nickel(II), en solution aqueuse, sont données. La solubilité du diméthylglyoximate de nickel, aux pH de 2 à 9 dépend de Ni^{+2} et $Ni(HDx)_2$; il ne semble pas que $NiHDx^+$ soit en quantité appréciable.

La constante d'extraction

$$\frac{[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}(a\mathrm{H^+})^2}{[\mathrm{Ni^{+2}}]\,[\mathrm{H_2Dx}]^2_{\mathrm{H_2O}}}$$

a été calculée à partir des constantes d'ionisation de $Ni(HDx)_2$ et H_2Dx, et des solubilités moléculaires du premier dans l'eau et le chloroforme.

ZUSAMMENFASSUNG

Es werden Werte für die Löslichkeitsproduktkonstante und die Ionisationskonstante von Nickel-II-dimethylglyoxim in wässriger Lösung berichtet. Für die Löslichkeit von Nickeldimethylglyoxim in dem untersuchten pH Bereich von 2 bis 9 werden die beiden Ionenarten Ni^{+2} und $Ni(HDx)_2$ verantwortlich gemacht. Es liegt kein Beweis vor für das Bestehen einer bedeutenden Menge $NiHDx^+$. Die Extraktionskonstante

$$\frac{[\mathrm{Ni(HDx)_2}]_{\mathrm{CHCl_3}}(a\mathrm{H^+})^2}{[\mathrm{Ni^{+2}}]\,[\mathrm{H_2Dx}]^2_{\mathrm{H_2O}}}$$

wurde aus den Ionisationskonstanten von $Ni(HDx)_2$ und H_2Dx und der molekularen Löslichkeit des ersteren in Wasser und Chloroform berechnet.

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CONTRIBUTION A L'ÉTUDE DE LA STANDARDISATION DES SOLUTIONS ACIDES NORMALES

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INTRODUCTION

La détermination précise du titre des solutions étalons constitue un des problèmes majeurs de la titrimétrie. En théorie, il s'agit de fixer expérimentalement d'une façon exacte la concentration d'un ion capable d'intervenir dans une réaction dont, d'autre part, on possède le moyen de reconnaître le terme.

Cette nécessité marque la dépendance de la titrimétrie vis-à-vis de la gravimétrie, celle-ci n'étant qu'une simple application de la loi des proportions définies. Appliqués à l'acidimétrie, les trois moyens dont on dispose sont: 1°) la pesée d'un acide déterminé, 2°) la détermination de l'anion de l'acide utilisé, 3°) la détermination du cation $(H)^+$.

Le premier moyen qui est le plus logique exige que le corps choisi présente un ensemble de qualités difficiles à réunir. Aussi, malgré le nombre considérable de corps proposés, aucun jusqu'à maintenant ne paraît avoir réussi à s'imposer pour la préparation d'une solution acide étalon.

Le deuxième moyen est d'un usage traditionnel (dosage des ions SO_4^{-2} pour la détermination du titre d'une solution acidimétrique normale). Il est basé, lui aussi, sur la loi des proportions définies, mais suppose que l'acide utilisé est pur.

Le troisième moyen, au contraire, fait intervenir précisément l'ion $(H)^+$ dont l'union avec l'ion $(OH)^-$ opposé est la base même de l'acido-alcalimétrie. Autrement dit, pour déterminer le poids d'ion $(H)^+$ contenu en solution, il faut connaître avec précision le poids de base susceptible de le neutraliser par ses ions $(OH)^-$. Cette méthode, pour le cas d'une solution acide étalon, ne préjuge pas de la nature des anions liés à l'hydrogène.

Malgré leur simplicité apparente, ces deux derniers moyens se heurtent à de nombreuses difficultés, comme l'a montré assez récemment LASSIEUR[1,2]. C'est parce que nous avons eu à les résoudre dans le laboratoire où nous poursuivons nos recherches depuis une dizaine d'années avec divers collaborateurs, que nous avons été amenés à examiner de plus près le problème. Nous résumons nos obser-

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vations anciennes concernant un certain nombre de méthodes classiques et nous proposons une technique qui nous paraît présenter un certain nombre d'avantages.

EXAMEN CRITIQUE DES PRINCIPALES MÉTHODES UTILISÉES

Nous limiterons cet examen à celui des diverses méthodes de dosage des solutions d'acide sulfurique.

A. MÉTHODES PAR DÉTERMINATION DE L'ANION DE L'ACIDE

Les deux méthodes les plus répandues sont celles au sulfate de baryum et celle au sulfate d'ammonium.

Méthode au sulfate de baryum

Comme on le sait, la méthode au sulfate de baryum a soulevé de très nombreuses controverses.

a. Principales critiques formulées

Bien que d'apparence simple, cette méthode présente un certain nombre de difficultés dont les principales sont: réduction partielle du sulfate de baryum au cours de la calcination du filtre sur lequel il est recueilli, surcharge due à la silice cédée éventuellement par le creuset dans lequel est effectuée la calcination, adsorption de chlorure de baryum sur le précipité de sulfate.

b. Examen de ces critiques

Un certain nombre des causes d'erreurs signalées peuvent être évitées en modifiant légèrement le protocole habituel.

a) *Erreurs dues à la calcination.* Ces erreurs peuvent être facilement éliminées en supprimant la calcination qui n'est pas indispensable. Le mode opératoire est alors légèrement modifié. Nous le relaterons dans ses grandes lignes.

La précipitation de l'acide sulfurique à l'état de sel de baryum est effectuée dans un bécher pyrex de 600 ml de capacité, en milieu suffisamment dilué, c'est-à-dire que la prise d'essai de 20 ml de la solution acide à doser est amenée à un volume d'environ 400 ml par addition d'eau distillée. Après cessation de l'addition de chlorure de baryum, effectuée goutte à goutte à l'ébullition, l'ébullition est prolongée jusqu'à ce que le précipité soit rassemblé au fond du bécher, la liqueur surnageante étant à peu près claire; ce résultat est atteint au bout de 45 à 60 minutes. Le bécher est alors abandonné pendant 12 heures à l'étuve à 37°.

Ces conditions opératoires permettent d'obtenir un précipité de sulfate de baryum dont les grains sont suffisamment gros pour qu'il puisse être recueilli sur un

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creuset filtrant G 4, lequel est ensuite desséché à une température au moins égale à 100°. En suivant un tel protocole opératoire, la calcination est évitée, d'autant plus que la dessiccation s'est révélée pleinement opérante.

β) Erreurs dues à la solubilité dans l'eau du sulfate de baryum. Si quelques auteurs ont cru pouvoir imputer à la solubilité dans l'eau du sulfate de baryum une part des erreurs observées, nous pensons pour notre part que ces erreurs sont très faibles et même négligeables.

Ainsi nous avons lavé le précipité de sulfate de baryum, recueilli sur creuset filtrant, à l'aide de 2 litres d'eau distillée. Les différences de poids observées après le lavage ont été de l'ordre de 1 mg pour 2.33 g environ de précipité et il est d'ailleurs possible de penser qu'elles ne sont pas entièrement dues à la dissolution du sulfate de baryum. Il est d'autre part à remarquer qu'elles sont bien moindres que celles que l'on pourrait attendre d'après la solubilité, pourtant faible, du sulfate de baryum, par suite probablement d'une vitesse de dissolution très petite.

γ) Erreurs dues à l'adsorption de Cl_2Ba sur le précipité. Mais si les erreurs que nous avons signalées précédemment peuvent être soit évitées, soit tenues pour négligeables, il n'en reste pas moins que le titre des solutions déterminé par cette méthode a toujours été trouvé supérieur de 8 à 13‰ à celui déterminé par la méthode au sulfate d'ammonium, ainsi que d'ailleurs l'a observé LASSIEUR[1].

De nombreux essais nous ont montré que la surcharge était due à la présence de chlorures adsorbés. En effet, des recherches de chlorures après fusion alcaline d'une fraction du précipité ont toujours été positives, quelque soit le soin apporté au lavage de ce précipité. Il nous est donc apparu comme nécessaire de toujours corriger le poids de sulfate de baryum trouvé en lui retranchant le poids de chlorure de baryum qu'il renferme, calculé d'après la quantité d'ion chlore dosée. Pour ce faire, nous disposons dans un creuset de porcelaine 3 à 4 grammes de carbonate de sodium anhydre vérifié exempt de chlorures, puis une quantité exactement déterminée et voisine de 1 g du précipité de sulfate de baryum recueilli. Nous recouvrons de 6 à 7 g de carbonate de sodium neutre anhydre, puis chauffons jusqu'à fusion complète de celui-ci. Nous laissons refroidir immédiatement et reprenons par l'eau distillée, la solution obtenue est neutralisée par addition d'acide nitrique concentré jusqu'à cessation de l'effervescence. Les chlorures sont alors dosés par la méthode classique de CHARPENTIER - VOLHARD.

Le titre des solutions sulfuriques ainsi déterminé d'après le poids de sulfate de baryum corrigé a toujours été voisin de celui trouvé par la méthode au sulfate d'ammonium, les différences étant de l'ordre de 2‰ d'accord avec les résultats obtenus par KAHANE ET KORACH[3]. Il convient cependant de souligner que les conditions opératoires influencent très nettement les résultats, comme d'ailleurs l'ont montré POPOFF ET NEUMAN[4].

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c. Conclusion

Il nous apparaît donc excessif de rejeter purement et simplement la méthode au sulfate de baryum, comme le préconise un certain nombre d'analystes. De bons résultats sont obtenus en prenant un certain nombre de précautions et notamment en tenant compte du chlorure de baryum adsorbé sur le précipité. Toutefois, l'utilisation de cette méthode est assez délicate et le dosage des chlorures, après fusion alcaline, est une opération ennuyeuse.

2. *Méthode au sulfate d'ammonium*

La méthode de dosage de l'acide sulfurique par pesée à l'état de sulfate d'ammonium a également donné lieu à des discussions. La divergence entre les résultats obtenus par divers auteurs semble provenir de la diversité des modes opératoires utilisés. Or les détails techniques de la méthode jouent un rôle déterminant dans la précision des résultats. FLEURY fait utiliser avec succès cette méthode dans son laboratoire depuis 25 ans, mais des résultats précis et fidèles n'ont été obtenus qu'après avoir défini un protocole opératoire précis[5].

Un certain nombre de précautions sont nécessaires. Il faut vérifier que l'eau distillée et l'ammoniaque utilisées ne laissent pas de résidu à 100°, utiliser un cristallisoir de forme courante et de dimensions standard (70 à 90 mm de diamètre). Le choix d'un cristallisoir de dimensions déterminées est important. Si celui-ci est de trop petit diamètre, lors de l'évaporation, de petites poches de liquide restent incluses dans le résidu cristallisé. D'un autre côté, il est nécessaire d'opérer cette évaporation au bain-marie avant de porter à l'étuve à 100°. En effet, lors d'une évaporation trop brutale, le sulfate d'ammonium a tendance à grimper le long des parois du récipient. Enfin, la température de l'étuve ne doit pas excéder notablement 105°. En effet, lorsque nous avons effectué la dessiccation à l'étuve à 120°, nous avons observé des pertes notables d'ammoniac.

Enfin, une dernière précaution est souhaitable: elle consiste à déterminer l'ammoniac qui a pu être perdu par décomposition du sulfate d'ammonium lors de la dessiccation. Cette détermination peut être effectuée en mettant le résidu obtenu en solution dans 20 ml d'eau distillée et en titrant, par une solution d'hydroxyde de sodium $N/10$ en présence de rouge de méthyle, l'acide sulfurique libre contenu dans la solution. Le pH de celle-ci qui est en général compris entre 3.0 et 4.0 est ainsi ramené à une valeur voisine de 5.0 (virage à l'orangé de l'indicateur). Nous avons en effet constaté qu'une solution aqueuse renfermant 1.32 g de sulfate d'ammonium pur pour un volume de 20 ml avait un pH voisin de 5.3. Dans les cas défavorables, le volume de soude ajouté peut être de l'ordre de 1 ml.

En résumé, la technique au sulfate d'ammonium donne de bons résultats si certaines précautions sont observées. Ces résultats sont comparables à ceux obtenus par la technique au sulfate de baryum et elle est plus commode pour un usage courant.

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B. MÉTHODES PAR DÉTERMINATION DU CATION $(H)^+$

Si la technique au sulfate d'ammonium apparaît comme satisfaisante, il n'en reste pas moins que de nombreux auteurs s'accordent pour reconnaître qu'il est souhaitable, pour l'établissement du titre d'une solution étalon, de comparer les résultats obtenus par au moins deux techniques différentes. C'est ainsi qu'il était logique de rechercher une deuxième technique parmi celles basées sur la détermination du cation $(H)^+$.

Comme nous l'avons déjà signalé, c'est le choix de la base de référence qui constitue la partie délicate. Parmi les nombreuses bases proposées par différents auteurs, le carbonate neutre de sodium a particulièrement retenu notre attention.

LASSIEUR[6] a d'ailleurs proposé comme étalon International en acidimétrie une solution d'acide sulfurique titrée par rapport au carbonate neutre de sodium anhydre.

1. *Emploi du carbonate de sodium comme élément de référence*

La technique de LASSIEUR[6] qui selon les résultats obtenus par KAHANE ET KORACH[3] est précise, semble cependant présenter un certain nombre d'inconvénients. Elle nécessite en premier lieu de posséder un échantillon de carbonate neutre de sodium purissime, ce qui rend la précision de la méthode tributaire de certaines marques de produits bien définis. Nous avons pensé qu'il était de beaucoup préférable d'utiliser, si possible, une technique basée sur l'utilisation de produits d'une pureté courante.

D'un autre côté, les produits du commerce, même purissimes, sont susceptibles de renfermer de petites quantités d'eau. C'est pourquoi LASSIEUR[6] a été amené à recommander l'utilisation d'un carbonate de sodium préalablement calciné dans une capsule de platine. Cet auteur ne donne pas de conditions opératoires bien définies pour la calcination, la seule condition indiquée étant que le sel ne devait pas fondre. Cette lacune a d'ailleurs été mise en évidence par DUPUIS ET DUVAL[7]. D'un autre côté, SMITH ET CROAD[9] ont montré que le carbonate de sodium anhydre se dissocie pour libérer du CO_2 à partir d'une température de 300°, résultats qui d'ailleurs ne s'accordent pas avec ceux de WALDBAUER, MCCANN ET TULEEN[9] dont les résultats montrent que le carbonate neutre de sodium peut être chauffé sans altération jusqu'à 475°. Les résultats de ces divers auteurs étant contradictoires, en apparence tout au moins, il nous a paru intéressant d'étudier l'influence de la température de chauffage sur la transformation du bicarbonate de soude en carbonate neutre de sodium. En effet, ces derniers auteurs ont établi leurs conclusions d'après du carbonate neutre de sodium obtenu par calcination de l'hydrogénocarbonate de sodium, alors que LASSIEUR utilisait du carbonate neutre de sodium du commerce.

a. *Etude de la calcination de l'hydrogénocarbonate de sodium*

Nous nous sommes placés volontairement dans des conditions expérimentales

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relativement simples, contrairement à celles de SMITH ET CROAD[8] qui ont utilisé un appareillage non courant dans les laboratoires.

L'hydrogénocarbonate de sodium utilisé a été obtenu en purifiant le produit commercial par lavage sur buchner à l'aide d'une solution saturée d'hydrogénocarbonate de sodium de même provenance. Le produit a été ensuite abandonné à la température du laboratoire jusqu'à poids constant. De cette façon, nous avons pu obtenir un échantillon très pur.

Des prises d'essai de ce produit, voisines de 2.2 g, ont été disposées dans une capsule de platine à fond rond d'environ 40 mm de diamètre, et chauffées à des températures variables au four électrique. Nous avons noté la perte de poids observée au cours du chauffage, la capsule étant pesée avant et après chauffage dans une boîte de verre fermée de manière à éviter toute influence du CO_2 de l'atmosphère. Les résultats obtenus ont été rassemblés dans le Tableau I.

TABLEAU I

PERTE DE POIDS PAR CHAUFFAGE DE L'HYDROGÉNOCARBONATE DE SODIUM (EN POURCENTAGES)

Temps (en heures)	Températures								
	100°	140°	180°	275°	330°	410°	530°	730°	825°
0.5	13.74	34.42	36.57	36.66	36.75	36.80	36.85	36.88	37.43
1	15.73	36.63	36.65	36.70	36.77	36.86	36.88	36.97	38.30
2	36.65	36.66	36.68	36.72	36.78	36.88	36.90	36.99	42.63
4	36.68	36.69	36.70	36.75	36.81	36.90	36.93	37.00	71.91

Perte de poids pour la transformation théorique de l'hydrogénocarbonate de sodium en carbonate de sodium: 36.94%

b. Etude critique de l'emploi de l'hydrogénocarbonate de sodium pour l'obtention d'un échantillon purissime de carbonate neutre de sodium

De l'examen des résultats obtenus, il résulte que dans les conditions précisées précédemment la perte de poids par chauffage de notre échantillon d'hydrogénocarbonate de sodium ne correspond à la transformation théorique en carbonate de sodium que pour un écart de température de chauffage assez étroit compris approximativement entre 450 et 550°. Ces conclusions sont apparemment en opposition avec les résultats obtenus par les différents auteurs déjà cités, qui déjà étaient discordants entre eux.

Il paraît logique de penser que les divergences sont dues aux différences existant dans les conditions opératoires. Il est vraisemblable que le facteur déterminant est la proportion de CO_2 présente dans l'air atmosphérique qui se trouve au contact du sel au cours de la calcination.

Dans ces conditions, on serait tenté d'admettre que la stabilité du carbonate de sodium vis-à-vis du chauffage n'est pas la même suivant qu'il s'agit du chauffage

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du carbonate de sodium lui-même ou du carbonate neutre de sodium obtenu par calcination du bicarbonate. A certaines températures, pourtant inférieures à celles pour lesquelles on observe une décomposition du carbonate neutre, une petite partie de l'hydrogénocarbonate serait décomposée sans passer par le stade carbonate neutre.

c. Conclusion

Devant ces incertitudes et ces contradictions, nous avons été amenés à rechercher s'il ne serait pas possible d'utiliser l'hydrogénocarbonate de potassium, produit qui se présente sous forme très bien cristallisée, et dont les échantillons commerciaux sont habituellement très purs. Les résultats obtenus nous ont permis de mettre au point une technique pour l'étalonnage des solutions acides basée sur l'utilisation de l'hydrogénocarbonate de potassium, après transformation quantitative de celui-ci en carbonate dipotassique.

D'ailleurs on pouvait se demander s'il ne serait pas possible de peser directement l'hydrogénocarbonate de potassium. Cette solution avait été proposée par BOUGAULT. Seule la crainte de petites variations fortuites résultant de l'instabilité des hydrogénocarbonates nous a empêchés de l'adopter.

2. Technique proposée

Principe

L'hydrogénocarbonate de potassium, calciné dans des conditions bien déterminées, est transformé quantitativement en carbonate neutre de potassium. La base ainsi obtenue est utilisée pour déterminer le titre exact d'une solution acide.

Matériel nécessaire

1. *Bain de sable:* le dispositif nécessaire peut être très simplement réalisé de la façon suivante:

Une capsule est remplie aux trois quarts de sable de Fontainebleau* et disposée directement sur un trépied. Un thermomètre, maintenu par un support, est disposé de telle façon que le réservoir de mercure plonge de 1 à 2 cm dans le sable.

La capsule est chauffée à feu nu à l'aide d'un bec bunsen dont la flamme est réglée de manière à ce que le niveau du mercure se stabilise entre les divisions 300 et 350. Le bain de sable est alors prêt à être utilisé.

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* A titre indicatif, la température désirée est facilement atteinte en utilisant 400 g de sable dans une capsule en fer émaillée dont les dimensions sont: hauteur: 7.5 cm, diamètre: 6 cm (fond), 15.8 cm (bord supérieur) ou 375 g de sable dans une capsule de hauteur: 5 cm, diamètre: 5 cm (fond), 11 cm (bord supérieur).

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2. *Erlenmeyer*: les meilleurs résultats sont obtenus en utilisant un erlenmeyer bouché émeri de 150 ml en verre pyrex, et préalablement passé au mélange sulfochromique puis rincé 2 à 3 fois à l'aide d'eau distillée. (Verifier la neutralité au tournesol de l'eau après rinçage.)

3. *Pipette*: il est nécessaire d'utiliser une pipette de 20 ml dont la capacité a été vérifiée d'après l'eau écoulée.

4. *Burette*: on peut utiliser une burette graduée en vingtièmes de centimètre cube, mais une microburette graduée en cinquantièmes ou en centièmes de ml est préférable.

Réactifs

1. *Hydrogénocarbonate de potassium:* produit pur du commerce préalablement pulvérisé au mortier.

2. *Indicateur*

Méthylorange	0.050 g
Vert de bromocrésol	0.250 g
Alcool absolu	50 ml

Triturer au mortier jusqu'à dissolution et ajouter 50 ml d'eau distillée.

Cet indicateur, bleu vert foncé en milieu alcalin, vire au vert jaune, puis à la teinte Champagne pour devenir rose en milieu fortement acide. (pH de virage: 4.1 correspondant à la teinte champagne).

Mode opératoire

Sur le bain de sable préparé comme il a été indiqué, l'erlenmeyer débouché est disposé de telle façon qu'il soit enfoncé d'environ 1 cm dans le sable. Il est chauffé ainsi pendant 1/2 heure. Le bouchon de l'erlenmeyer est mis pendant ce temps à l'étuve à 100°.

Erlenmeyer et bouchon sont alors portés dans un dessiccateur à vide *garni d'acide sulfurique*, le robinet du dessiccateur étant ouvert. Fermer ce robinet au bout de 2 minutes environ.

Après 1/2 heure, l'erlenmeyer est revenu à la température ambiante. Le retirer du dessiccateur, lui adapter aussitôt son bouchon et éliminer rapidement les grains de sable qui peuvent adhérer aux parois en promenant le long de celles-ci le bord d'un morceau de papier filtre bien sec.

Tarer rapidement sur une balance sensible au 1/10 mg. Peser d'autre part au trébuchet entre 2.2 et 2.3 g d'hydrogénocarbonate de potassium et introduire cette quantité dans l'erlenmeyer en ayant soin d'étaler le plus possible le produit sur le fond du récipient*.

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* Il est inutile de déterminer exactement le poids ainsi introduit. Seul le poids du corps obtenu *après calcination* intervient pour la détermination.

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Calciner au bain de sable pendant 2 heures en disposant l'erlenmeyer comme il a été dit précédemment. Pendant ce temps, reporter le bouchon à l'étuve à 100°.

Au bout des 2 heures de calcination, introduire séparément erlenmeyer et bouchon dans le dessiccateur en procédant comme il a été déjà indiqué. L'erlenmeyer, coiffé de son bouchon, est alors taré à nouveau 1/2 heure après sur la balance sensible au 1/10 de mg. Noter le poids p du résidu (CO_3K_2) ainsi obtenu.

Introduire ensuite dans l'erlenmeyer 10 ml d'eau distillée. Agiter pour dissoudre la majeure partie du carbonate neutre de potassium, puis ajouter à la pipette, lentement et en agitant, 20 ml de la solution acide à titrer, puis 2 gouttes de la solution d'indicateur. Laver les parois internes du récipient à l'aide de petits jets de pissette contenant de l'eau distillée.

Verser alors goutte à goutte, à la burette, une nouvelle quantité de solution à titrer jusqu'à virage de l'indicateur à la teinte champagne.

Calcul

$$\text{Soient} \begin{cases} p \text{ g le poids de carbonate de potassium mis en jeu,} \\ n \text{ ml le volume de solution acide versée à la burette,} \end{cases}$$

$$\text{Titre de la solution (en normalité)} = \frac{1000\, p}{69\,(n+20)}$$

Il est recommandé d'adopter comme résultat la moyenne de 2 déterminations.

Etude critique

1. *Choix de l'échantillon d'hydrogénocarbonate de potassium.* Des essais effectués en utilisant des échantillons d'hydrogénocarbonate de potassium d'origines très diverses, il ressort qu'il n'est pas nécessaire d'employer un réactif purissime pour analyses. Tous les produits du commerce que nous avons employés, étiquetés ,,bicarbonate de potassium cristallisé pur'', nous ont donné de bons résultats.

2. *Choix du récipient pour la calcination:* le carbonate neutre de potassium anhydre tend à capter l'humidité atmosphérique, c'est pourquoi nous avons choisi un récipient clos pour effectuer la pesée.

Nos premiers essais ont été effectués en utilisant une capsule en platine ou une capsule en argent. Pour la pesée, ces capsules étaient placées dans une boîte de verre. Nous nous sommes rendus compte que la capsule pouvait être pesée à l'air à condition que l'opération soit faite très rapidement. Ceci nous a incité à refaire les dosages en utilisant des récipients d'un prix de revient moins élevé: erlenmeyer non bouché en pyrex, bécher en pyrex, capsule en porcelaine vernissée. Aucune différence dans les résultats des dosages n'a été observée.

C'est ainsi que nous avons été amenés à adopter pour la calcination un récipient pyrex: erlenmeyer ou bécher, matériel courant dans les laboratoires et qui présente l'avantage de permettre d'effectuer le titrage dans le récipient qui a servi pour la calcination. Nous croyons cependant devoir recommander l'utilisation d'un erlenmeyer bouchant émeri, car la pesée d'un récipient non clos doit être effectuée extrêmement rapidement si l'on veut éviter les erreurs, ce qui demande une grande habileté expérimentale et une balance à lecture rapide.

3. *Précautions à prendre pour les pesées.* Des essais ont montré que si les pesées sont effectuées en un temps suffisamment court, soit moins de 3 minutes, il est inutile de laisser séjourner le récipient pendant 15 minutes dans la chambre de la balance avant de peser. Les erreurs sont alors négligeables.

4. *Temps et température de calcination.* Un échantillon purissime d'hydrogénocarbonate a été soumis au chauffage pendant des temps et à des températures variables. Les conditions opératoires ont été les mêmes que celles utilisées pour étudier la décomposition thermique de l'hydrogénocarbonate de sodium.

Les résultats obtenus, qui font l'objet du Tableau II, montrent qu'en-dessous de 250° la transformation de l'hydrogénocarbonate en carbonate neutre est lente. Par contre, en le chauffant à une température supérieure à 400°, l'hydrogénocarbonate de potassium subit une perte de poids supérieure à celle correspondant à la transformation théorique en carbonate neutre.

Pour obtenir la base destinée au titrage d'une solution acide, de bons résultats seront donc obtenus en opérant un chauffage de 2 heures de l'hydrogénocarbonate de potassium à une température comprise entre 250° et 350°.

TABLEAU II

PERTE DE POIDS PAR CHAUFFAGE DE L'HYDROGÉNOCARBONATE DE POTASSIUM (EN POURCENTAGES)

Temps (en heures)	Températures (en degrés centigrades)									
	100°	140°	180°	275°	330°	410°	530°	730°	825°	935°
0.5	—	9.02	29.00	30.81	30.83	30.85	31.06	31.16	31.64	32.79
1	0.28	13.69	30.28	30.85	30.87	30.90	31.08	31.18	31.93	34.65
2	0.36	22.02	30.70	30.88	30.93	31.01	31.10	31.21	32.87	39.12
4	0.39	23.70	30.76	30.89	30.94	31.02	31.11	31.24	—	—
8	—	30.72	30.78	30.90	30.94	31.03	31.12	31.55	—	—
24	1.84	30.79	30.80	30.96	30.98	31.04	31.24	31.78	—	—

Perte de poids pour la transformation théorique du bicarbonate de potasse en carbonate neutre de potassium = 31.00

5. *Rapport entre le „pouvoir titrant" et la température de chauffage de l'hydrogénocarbonate de potassium.* Afin d'appuyer les conclusions du paragraphe précédent sur des bases encore plus solides, il nous a paru intéressant de montrer qu'il y a bien correspondance entre la perte de poids par chauffage de l'hydrogéno-

carbonate de potassium et le „pouvoir titrant" du produit obtenu. Pour ce faire, nous avons déterminé le titre d'une solution exactement normale d'acide sulfurique en suivant la technique déjà exposée, à la seule différence près qu'au lieu d'opérer la calcination au bain de sable, nous avons opéré sur les produits obtenus dans les conditions de l'expérience précédente, par chauffage pendant 2 heures à des températures variables. Les résultats représentés par la figure I montrent que le „pouvoir titrant" du produit obtenu est théorique pour une température de chauffage comprise entre 250° et 350°. Un chauffage de 2 heures à une température inférieure à 250° conduit à des résultats trop élevés, alors que si la température dépasse 400° ceux-ci sont trop faibles. Si l'on se reporte au Tableau II, on voit que dans le premier cas la perte de poids est inférieure à la théorie et dans le second cas supérieure. Il y a donc bien correspondance entre le „pouvoir titrant" et la température de chauffage du bicarbonate de potasse, tout au moins dans les limites choisies pour obtenir la base utilisée dans le dosage.

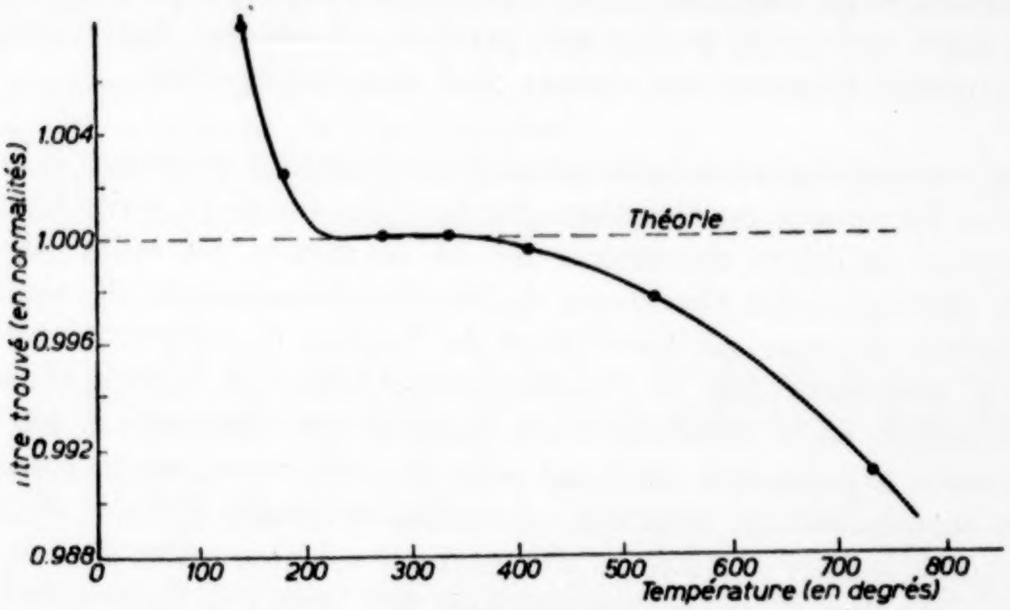

Fig. 1

Variations du „pouvoir titrant" en fonction de la température de chauffage de l'hydrogénocarbonate de potassium
Abscisses: température de chauffage de l'hydrogécarbonate de potassium
Ordonnées: résultats du dosage (en normalités) d'une solution d'acide sulfurique *N*/1

D'un autre côté, cette expérience montre que la marge de température de chauffage que nous avons fixée entre 250° et 350° est suffisante puisque les résultats obtenus pour des températures comprises entre 175° et 475° ne s'écartent pas de plus de $1^0/_{00}$ du résultat théorique.

6. *Choix de l'indicateur.* L'utilisation d'un indicateur dont le pH de virage est situé en zône acide permet d'éviter les erreurs dues à la présence d'acide

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carbonique dans le milieu sans qu'il soit nécessaire de l'éliminer par chauffage comme le préconise LASSIEUR[5]. D'autre part, nous avons adopté un indicateur composé [10] dont le virage est plus facile à saisir que celui du méthylorange employé seul.

7. *Précision des résultats.* Afin d'apprécier la précision des résultats, nous avons effectué des dosages sur des solutions de titre variable obtenues par dilution d'une même solution mère ajustée exactement à la normalité selon la technique proposée.

Les résultats du Tableau III montrent que lorsqu'on prend pour titre d'une solution la valeur moyenne de 2 déterminations, l'erreur relative est inférieure à 2 p. 1000, celle-ci variant de 0.1 à 1.8 p. 1000. D'autre part, les écarts observés entre les résultats de déterminations effectuées sur une même solution varient de 0 à 1.6 p. 1000, l'écart moyen étant de 0.6 p. 1000.

La précision des résultats apparaît donc comme pleinement satisfaisante et au moins égale à celle obtenue en utilisant n'importe laquelle des techniques préconisées jusqu'à maintenant.

TABLEAU III

DÉTERMINATION DU TITRE DE DIVERSES SOLUTIONS D'ACIDE SULFURIQUE ET D'ACIDE CHLORHYDRIQUE

Titre de la solution de SO_4H_2 dosée (en normalités)			Titre de la solution de ClH dosée (en normalités)		
Trouvé		Théorie	Trouvé		Théorie
Résultats individuels	Moyenne		Résultats individuels	Moyenne	
0.9996 — 1.0004	1.0000	1.000	0.9999 — 1.0009	1.0004	1.000
0.9944 — 0.9944	0.9944	0.995	0.9957 — 0.9960	0.9958	0.995
0.9899 — 0.9893	0.9896	0.990	0.9943 — 0.9943	0.9943	0.993
0.9863 — 0.9849	0.9856	0.985	0.9886 — 0.9894	0.9890	0.990
0.9802 — 0.9804	0.9803	0.980	0.9898 — 0.9896	0.9897	0.990
0.9759 — 0.9749	0.9754	0.975	0.9850 — 0.9852	0.9851	0.985
0.9699 — 0.9704	0.9701	0.970	0.9803 — 0.9803	0.9803	0.980
0.9653 — 0.9653	0.9653	0.965	0.9769 — 0.9759	0.9764	0.975
0.9607 — 0.9597	0.9602	0.960	0.9713 — 0.9704	0.9708	0.970
0.9505 — 0.9504	0.9504	0.950	0.9599 — 0.9607	0.9607	0.960

8. *Comparaison des résultats obtenus par cette technique et ceux obtenus en utilisant les techniques gravimétriques.* Dans la première partie de notre exposé, nous avons signalé que la technique de dosage de l'acide sulfurique à l'état de sulfate de baryum donne des résultats concordant avec ceux obtenus par la méthode au sulfate d'ammonium, à condition que les opérations soient conduites

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suivant un protocole opératoire bien défini. Les résultats du Tableau IV montrent également qu'il y a concordance entre le titre d'une solution d'acide sulfurique déterminé par la méthode au sulfate d'ammonium et celui déterminé par la méthode que nous proposons. Les différences observées sont au plus égales à 2 p. 1000.

TABLEAU IV

DÉTERMINATION DU TITRE DE DIVERSES SOLUTIONS SULFURIQUES PAR LA MÉTHODE AU SULFATE D'AMMONIUM ET PAR NOTRE TECHNIQUE UTILISANT L'HYDROGÉNOCARBONATE DE POTASSIUM

	Titre trouvé (en normalités)		
Méthode au sulfate d'ammonium	0,983	0.998	0.993
Méthode proposée	0.984	1.000	0.995

Nous remercions le Professeur P. Fleury pour l'intérêt qu'il a bien voulu prendre à ce travail.

RÉSUMÉ

Une méthode à la fois très commode et très précise est proposée pour l'établissement des solutions normales acides. L'hydrogénocarbonate de potassium est transformé par calcination en carbonate neutre de potassium. La base ainsi obtenue est utilisée pour la détermination du titre des solutions acides selon un protocole opératoire qui est précisé. Ces résultats sont obtenus avec une précision de 2 p. 1000.

Les principales techniques classiques font l'objet d'un examen critique.

SUMMARY

A very convenient and accurate method is proposed for titrating normal acid solutions. Potassium bicarbonate is converted through calcination into neutral potassium carbonate. The base thus obtained is used to determine the titre of acid solutions, following procedure clearly indicated. Results are obtained with an accuracy of 2 per 1000.

The main traditional methods are critically examined.

ZUSAMMENFASSUNG

Eine sehr bequeme und genaue Methode wird zur Titration normaler Säurelösungen vorgeschlagen. Kaliumbikarbonat wird durch Calcinierung in neutrales Kaliumkarbonat umgewandelt. Die so erhaltene Base wird zur Bestimmung des Titers von Säurelösungen nach dem genau angegebenen Verfahren verwendet. Die Ergebnisse werden mit einer Genauigkeit von 2 pro 1000 erhalten. Die hauptsächlichen traditionellen Methoden werden kritisch überprüft.

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THE TITRATION OF Al WITH COMPLEXONE III AT A pH 3.5

by

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INTRODUCTION

In a previous communication[2] we dealt with the titration of complexone III by means of thorium nitrate. In this way it is possible to titrate an excess of complexone III at pH 2.8-4.3 using alizarin S as an indicator.

Use of this reaction can be made in the determination of those metal ions which form complexes with complexone III at a pH of 2.8-4.3, simply by adding a known excess and back-titrating with thorium nitrate.

In this paper we will describe the determination of Al in this way.

As is known from the dissertation of BIEDERMANN[1], Al forms two complexes with complexone III (H_4Y), one at about pH 4.5 and another at pH about 8.5, according to the reactions[1]

a) $H_2O + Al^{+3} + H_2Y^{-2} \rightleftharpoons Al(OH)HY^{-} + 2H^{+}$ and

b) $Al(OH)HY^{-} \rightleftharpoons Al(OH)Y^{-2} + H^{+}$

As the whole of H_4Y is taken up by Al at about pH 4.5 (reaction a), the best way to titrate Al would be at this pH. In fact we did find that at lower pH the reaction did not go to completion, although even at pH 4.3 we found about 0.5% less Al than would be expected. It may be that this fact must be partly attributed to the reaction between Al-complexone and Th^{+4} ions, as it is clear from our experiments that the formation constant of Al-complexone is somewhat less than that of Th-complexone; but it is also shown that it depends to a certain extent on the slow reaction between Al and complexone.

The pH range in which the determination should be performed goes from 3.5 at room temperature to pH 4.3 at boiling temperature.

Below this the deviations amount to more than 3% and above pH 4.3 one gets difficulties in finding the end point on account of the increasing dark-orange colour of the solution.

As it has been pointed out, we did not succeed in titrating Al to 100%, but, working at pH 3.5, the deviation was about 1% low and was quite reproducible. So one can work with a complexone-solution, previously standardised by titration on pure zinc[2] and taking an about 1% higher factor for Al (1 meq = theoretically 13.49 mg Al).

In this way we obtained quite satisfactory results on a series of Al-alloys. At the end point the solution bleaches after about 5 minutes, probably on account of the competition between Al-complexone and thorium ions; this might make the method seem more or less untrustworthy, but in practice we did not have difficulties with this phenomenon.

PROCEDURE

To the solution which should contain about 1-4 milliequivalents of Al (about 10-50 mg of Al) in a volume of about 100 ml is added an excess of complexone III 0.05*M*. The solution is neutralised on a piece of congo red paper and then 5 ml monochloracetic acid 2*M* and 10 ml Na-acetate 1*M* are added.

The pH should be between 3.5 and 3.6.

Then $1\frac{1}{2}$ ml of alizarin S indicator 0.1% is added and the excess of complexone III is back-titrated with standard thorium nitrate solution 0.05*M*. The colour change is from orange to sudden red.

For a titration at pH 4.3 the solution is buffered with 10 ml acetic acid 2*M* and 10 ml Na-acetate 1*M*, heated to boiling and, after the addition of indicator solution, back-titrated with thorium nitrate. The colour change is less sharp and goes from dark-orange to red.

Theoretically 1 ml 0.05*M* complexone III is equivalent to 13.49 mg Al.

For practical purposes the best way is to determine the factor for Al on a series of exactly known quantities of Al.

SOLUTIONS

All reagents c.p. quality.

For the solutions deionised water should preferably be used.

a) Complexone III 0.05*M*:
    18.6 g of disodium salt of ethylenediaminetetra-acetic acid is dissolved and diluted to 1 l.

b) Thorium nitrate 0.05*M*:
    27.6 g $Th(NO_3)_4.4H_2O$ is dissolved and diluted to 1 l.
    Both solutions are standardised according to the method described in an earlier publication[2].

c) Alizarin S indicator 0.1%:
    100 mg alizarin S is dissolved and diluted to 100 ml.

d) Monochloracetic acid 2*M*:

189 g $CH_2ClCOOH$ is dissolved and diluted to 1000 ml.

e) Sodium acetate 1*M*:

136 g $CH_3COONa.3H_2Oa$ is dissolved and diluted to 1000 ml.

EXPERIMENTAL

For our experiments on pure solutions of Al, we used 99.99% Al which was dissolved in aqua regia and diluted to an appropriate volume. The solution, which should contain 21.06 mg Al in 5 ml, was checked gravimetrically by the oxine method; we found 21.10 and 21.15 mg Al per 5 ml, a deviation which is within the experimental error of the method.

From this standard solution we took about 10, 20 and 40 mg Al, which were titrated at a pH of 3.5 and 4.3. To get some information about the reproducibility of the end point, the solutions at pH 3.5 were titrated according to the "forward-backward" method we also used in an earlier publication[2]; that is the solution is titrated with thorium nitrate, then more complexone is added and again titrated and so on, until 4 readings (with increments of about 5 ml) are obtained.

TABLE I

TITRATION OF Al AT pH 3.5 AND 4.3 WITH COMPLEXONE — THORIUM NITRATE, CALCULATED WITH THEORETICAL FACTOR FOR Al.

pH 3.5			pH 4.3		
mg Al present	mg Al found	deviation of $\overline{x}$ from true value in %	mg Al present	mg Al found	deviation from true value in %
	10.48		8.43	8.43	0
	10.41		10.53	10.42	—1.0
10.53	10.42	—1.0	21.06	20.97	—0.4
	10.37		42.13	41.83	—0.7
$\overline{x}$ =	10.42			mean	—0.5
	20.77				
	20.76				
21.06	20.77	—1.4	volume *ca.* 100 ml		
	20.80		10 ml HAc 2*M*		
			10 ml NaAc 1*M*		
$\overline{x}$ =	20.77		1.5 ml alizarin S		
			titrated at boiling temp.		
	41.57				
	41.52				
42.13	41.54	—1.4			
	41.57				
$\overline{x}$ =	41.55	mean —1.3			

volume *ca.* 100 ml
5 ml mono-ClAc 2*M*
10 ml NaAc 1*M*
1.5 ml alizarin S
titrated at room temp.

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The amount of Al was calculated from the total amount of complexone and thorium nitrate used in each titration, using the theoretical factor for Al (1 meq = 13.49 mg Al). From such a series one can easily calculate the practical factor.

In Table I some values are given which were obtained by this method on different amounts of Al at pH 3.5 and 4.3.

If the low results should be attributed to a slow reaction between Al and complexone, then it must be possible to get better results by warming the solution of Al and complexone during, say, about 1 hour before back-titrating.

In Table II the results of some experiments performed in this way are given.

TABLE II

TITRATION OF Al AT pH 3.5 AND 4.3 AFTER STANDING FOR 1 HOUR AT 70° C with EXCESS OF COMPLEXONE BEFORE BACK-TITRATING. CALCULATED WITH THEORETICAL FACTOR FOR Al.

pH 3.5			pH 4.3		
mg Al present	mg Al found	deviation in %	mg Al present	mg Al found	deviation in %
10.53	10.48	—0.5	10.53	10.52	—0.1
21.06	20.96	—0.5	21.06	20.96	—0.5
	20.92	—0.7			
42.12	41.76	—0.8	42.12	41.83	—0.7
		mean —0.6			mean —0.4

INTERFERENCES

As there are other metal ions that react at pH 3.5, some of them will interfere.

Of the cations we investigated, Fe, Ni and Bi react quantitatively; Mn interferes by giving an indistinct end point when present in amounts of more than 3 mg; and Co reacts similarly.

Cu, Pb, Zn and Cd interfere seriously but unfortunately do not react quantitatively.

There is no interference of Ca, Ba and Mg in amounts up to 40 mg.

Of the anions, fluorine, phosphate and oxalate interfere seriously by forming precipitates with thorium and partly by complexing Al. Sulfate also interferes when present in amounts of more than 2 meq; if more than 2 meq SO_4 are present, one can add a little $BaCl_2$ solution and filter ($BaSO_4$ does not interfere but tends to adsorb some of the indicator).

Chloride, nitrate and perchlorate do not interfere.

RESULTS ON Al-ALLOYS

As a check on the method, four standard Al-alloys of known composition were analysed as to their Al-content by the method described.

As the samples contained some iron which also reacts, we corrected the Al content for the Fe content (1 meq Fe = 27.92 mg Fe). No corrections for other elements present were made.

The samples were dissolved in aqua regia, diluted to a definite volume and a suitable aliquot taken. Titrations were performed at pH 3.5 using a practical factor for Al, previously determined on known amounts of Al.

In Table III the results are given.

TABLE III

RESULTS ON 4 Al-ALLOYS ANALYSED ON THEIR Al CONTENT. CORRECTION FOR Fe. TITRATION AT pH 3.5 WITH PRACTICAL FACTOR FOR Al.

% Al present	% Al found*	deviation of mean from true value in %	remarks			
90.5	90.4 90.8	+0.1	Si 0.2	Mg 8.8	Mn 0.2	Fe 0.3
86.1	86.0 85.8	—0.2	Si 12.7	Mg 0.4	Mn 0.4	Fe 0.4
96.8	96.3 96.8	—0.25	Si 1.1	Mg 0.8	Mn 0.8	Fe 0.5
95.8	95.5 95.5	—0.3	Si 0.2 Sb 0.1	Mg 2.7	Mn 1.0	Fe 0.2

* The first values of % Al found by analyst A, the second by analyst B.

DISCUSSION

As can be seen from Tables I and II there is evidence of a slow reaction between Al and complexone. This should partly explain the low results; because, when working at pH 3.5 or 4.3, there is no significant difference between the results when one waits about one hour before back-titrating the complexone. The effect of the 0.5% low results has not yet been explained but we think it should be attributed to the reverse reaction between Th^{+4} and Al-complexone, although one should expect a more pronounced effect when working at boiling temperature and as can be seen from the results there is no evidence of that.

Fortunately the low results at both pH are quite reproducible, and when working with a practical factor we have not yet encountered erratic results.

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One of the drawbacks of the method is the interference of SO_4, but addition of $BaCl_2$ eliminates this.

It is possible to titrate Fe and Al at the same time; first Fe is titrated at pH 2 (at which pH Al does not react) with complexone and rhodanide as an indicator and then an excess of complexone is added and back-titrated with thorium nitrate at pH 3.5 or 4.3.

One could standardise the complexone solution with pure Al, instead of taking the theoretical titer of complexone and adding about 1% for the Al-factor; but the drawback of this method is that increasing results for Al are obtained when the excess of complexone is increased. We therefore prefer the method described under the heading "Procedure", for then the results for Al become independent of the excess of complexone used.

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SUMMARY

A titration procedure for Al based on the reaction of Al and complexone III (disodium salt of ethylenediaminetetra-acetic acid, ("versene") at pH 3.5-4.3 is described. After adding an excess of complexone the excess is back-titrated with thorium nitrate, using alizarin S as an indicator. The reaction is not exactly stoichiometric, but nevertheless quite reproducible, and an about 1% higher factor for Al should be used.

RÉSUMÉ

Les auteurs décrivent une méthode de dosage de l'aluminium, basée sur la réaction avec le complexon III (sel disodique de l'acide éthylènediaminotétracétique) à un pH de 3.5 à 4.3. On utilise un excès de complexon que l'on titre en retour avec le nitrate de thorium, en présence d'alizarine S comme indicateur. La réaction n'est pas exactement stoechiométrique, mais elle est cependant tout à fait reproductible; on utilise un facteur de correction, les résultats trouvés doivent être augmentés de 1% environ.

ZUSAMMENFASSUNG

Es wird ein Titrationsverfahren für Aluminium beschrieben. das auf der Reaktion des Aluminiums mit Complexon III (Dinatriumsalz der Äthylendiamintetraessigsäure „Versene") bei pH 3.5-4.3 beruht. Nach dem Hinzufügen eines Überschusses von Complexon wird der Überschuss mit Thoriumnitrat zurücktitriert unter Benutzung von Alizarin S als Indikator. Die Reaktion ist nicht genau stöchiometrisch, aber trotzdem völlig reproduzierbar. Es sollte ein ungefähr um 1% höherer Faktor für Al benützt werden.

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LA SÉPARATION ET LE DOSAGE DU TUNGSTÈNE ET DU MOLYBDÈNE AU MOYEN DU CHLORURE DE CALCIUM

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Dans une série de minerais de molybdène que nous avons analysés, presque tous les échantillons étudiés contenaient du tungstène en des proportions variables. Nous avons donc été obligés de séparer le tungstène du molybdène.

On sait que les analogies entre les propriétés chimiques du tungstène et du molybdène[1] rendent leur séparation difficile[2].

Nous avons essayé les méthodes de HOMMEL[3], de ROSE[4] et de PÉCHARD[5]. Mais, ces méthodes exigeant de nombreuses précautions et d'autre part la durée de cette séparation n'étant pas toujours satisfaisante, nous avons cherché une méthode nouvelle, rapide et à la fois rigoureuse qui permette la séparation et le dosage gravimétrique des deux métaux.

Ayant vérifié qu'une solution de chlorure de calcium ajoutée à une solution de tungstate et de molybdate de sodium, provoque après quelques minutes d'ébullition, un précipité de tungstate et de molybdate de calcium, nous avons trouvé qu'en présence d'un excès de chlorure de calcium, le tungstate et le molybdate sont précipités quantitativement.

Les deux précipités étant insolubles dans l'eau, on peut donc les filtrer et les laver à l'eau. Cette possibilité nous a suggéré une méthode pour l'extraction du molybdène et du tungstène et par la suite, une pour leur dosage respectif.

Il est aisé d'obtenir le molybdate et le tungstate de sodium en traitant le minerai par une fusion alcaline avec un mélange de carbonate et de peroxyde de sodium. En traitant la masse fondue par de l'eau bouillante on parvient à extraire complètement le molybdène et le tungstène.

La méthode décrite pour la séparation des deux métaux est basée sur la formation de sels de calcium insolubles dans l'eau et par leur différence de solubilité dans l'acide chlorhydrique concentré. En effet, le tungstate de calcium est décomposé par l'acide chlorhydrique en chlorure de calcium et en acide tungstique qui précipite, alors que le molybdate de calcium est très soluble en se décomposant en chlorure de calcium et acide molybdique.

Par filtration à l'aide d'un creuset-filtre, on sépare quantitativement le tungstène du molybdène. L'acide tungstique est calciné jusqu'à poids constant et

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pesé comme le tri-oxyde de tungstène (WO_3). Il est aisé de calculer la teneur en tungstène.

Le molybdène est reprécipité sous forme de molybdate de calcium du filtrat précédent en le rendant alcalin et en chauffant à l'ébullition. On filtre à l'aide d'un creuset-filtre et l'on calcine le molybdate de calcium jusqu'à constance de poids.

Les essais pour sécher à 120° C le précipité recueilli dans un filtre de Gooch, n'ont pas donné des résultats satisfaisants, le précipité fraîchement obtenu devant être de composition indéterminée. Suivant les différences obtenues par le séchage et par calcination, nous devons admettre la perte d'une demi-molécule d'eau. Toutefois la littérature sur le molybdate de calcium ne mentionne pas la présence d'eau de cristallisation. Pour éviter une technique douteuse, nous avons eu recours à la calcination. Les résultats obtenus pour le tungstène et le molybdène sont reproduits dans le Tableau I. Nous avons utilisé à titre de vérification de notre méthode, du molybdate de sodium et du tungstate de sodium chimiquement purs. Les résultats obtenus (moyenne de deux essais) prouvent l'efficacité de la séparation et une détermination satisfaisante du molybdène et du tungstène.

TABLEAU I

No.	WO_3 g présent	WO_3 g trouvé	Mo g présent	Mo g trouvé
1	0.0070	0.0068	0.8267	0.8260
2	0.0350	0.0347	1.6534	1.6527
3	0.0700	0.0694	2.4801	2.4809
4	0.1050	0.1081	3.3068	3.3063
5	0.1400	0.1405	4.1335	4.1339
6	0.1750	0.1748	4.9602	4.9608
7	0.3500	0.3507	0.4134	0.4130
8	0.7000	0.6993	0.2067	0.2058
9	1.4000	1.4008	0.1038	0.1043
10	2.8000	2.7993	0.0620	0.0627
11	3.5000	3.5010	0.0311	0.0307
12	4.2000	4.1990	0.0150	0.0153

TECHNIQUE ADOPTÉE

1 g de minerai finement pulvérisé est introduit dans un creuset de platine. On ajoute comme mélange de fusion et d'oxydation* 1 g de carbonate de sodium anhydre et 6 g de peroxyde de sodium et l'on mélange le contenu du creuset à l'aide d'un fil de platine. On chauffe doucement au début sur un bec Mecker et

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* Les séparations du molybdène et du tungstène sont parfaites lorsque ces métaux sont à leur valence maximum, c'est-à-dire, à la valence 6.

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une fois la masse fondue, on augmente l'intensité de la flamme. On laisse ainsi jusqu'à l'obtention d'une masse complètement liquide.

Après refroidissement, on reprend le contenu du creuset par de l'eau bouillante contenue dans une capsule de porcelaine. On y introduit aussi le couvercle du creuset et l'on couvre la capsule pour éviter des projections. On chauffe pour mieux dissoudre les parties adhérentes aux parois du creuset et au couvercle. On ajoute de l'eau pour diluer la solution et l'on filtre. Filtre et précipité sont lavés plusieurs fois à l'eau chaude. Le précipité est écarté.

Le filtrat contient le tungstène et le molybdène sous forme de tungstate et de molybdate de sodium. Il est additionné d'acide chlorhydrique pour amener le pH à 8. Si nécessaire, on réduit le volume du bécher à ∼200 ml, par évaporation. Au liquide amené à l'ébullition, on ajoute 50 à 60 ml de glycérine chimiquement pure pour empêcher quelque adhérence possible aux parois du bécher, du précipité que l'on provoque par l'addition de 20-25 ml d'une solution saturée de chlorure de calcium.

On laisse bouillir pendant 2-3 minutes, évitant l'emploi d'une baguette de verre après l'addition du chlorure de calcium. Une autre précaution importante est l'emploi de verres sans les moindres défauts (égratigures, adhérences, etc.), car ceux-ci agiraient comme foyers de cristallisation en provoquant une forte adhérence des précipités, difficiles à enlever même à l'aide d'un policier.

Les précipités de tungstate et de molybdate de calcium sont filtrés puis lavés plusieurs fois avec de l'eau chaude contenant 5% de chlorure de calcium. Les précipités sont ôtés du filtre à l'aide d'une pissette à eau chaude et introduits dans un bécher. Le volume est réduit à 100 ml environ par évaporation et l'on y additionne 100 ml d'acide chlorhydrique concentré. Ce mélange est amené à ébullition, en le remuant à l'aide d'une baguette de verre pour permettre à l'acide d'attaquer complètement les précipités. Le molybdate de calcium passe en solution et il reste le précipité jaune de l'acide tungstique.

L'acide tungstique, filtré à la trompe au moyen d'un creuset-filtre, est lavé à l'eau chaude. On sèche le précipité et on le calcine au rouge (800° C) jusqu'à poids constant et l'on pèse le tri-oxyde de tungstène. Désirant obtenir le résultat en pourcentage de tungstène, on multiplie le poids de WO_3 par 79.31.

Le filtrat est soigneusement versé dans un bécher de 600 ml; on lave plusieurs fois le flacon de filtration (KITISATO) en réunissant les eaux de lavage au filtrat. On évapore ce dernier pour avoir un volume d'environ 100 ml. On introduit quelques gouttes de phénolphtaléine et l'on ajoute au liquide en ébullition de l'ammoniaque (en prenant soin d'éviter des projections), jusqu'à ce que la solution vire au rouge. On continue à bouillir pendant 2-3 minutes pour permettre la formation totale du molybdate de calcium. Nous rappellons qu'il ne faut pas utiliser de baguette de verre pendant et après l'addition de l'ammoniaque et il est indispensable que le bécher soit sans rayures.

Laisser refroidir pour que le précipité se dépose. Il est filtré à la trompe à

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l'aide d'un creuset en porcelaine à fond poreux. Le laver 3-4 fois à l'eau chaude contenant 5% de chlorure de calcium, puis deux fois avec de l'eau distillée. Le précipité est séché et ensuite calciné à une température entre 800 et 850° C. Lorsque le poids du molybdate de calcium est constant, on note le résultat. Celui-ci multiplié par 47.98 donne le pourcentage de molybdène contenu dans l'échantillon.

CONCLUSIONS

Nous nous sommes servis de la méthode décrite pour déterminer le molybdène et le tungstène dans les minerais de molybdène tels que la molybdénite, la wulfénite et la powellite. C'est surtout avec ce dernier que la méthode s'est montrée très intéressante. En effet la teneur en tungstène est plus grande que dans les autres minerais de molybdène. La séparation est très bonne et la détermination du tungstène très satisfaisante. La méthode utilisée permet la séparation et la détermination gravimétrique des deux métaux en une journée.

Nous avons fait également quelques essais avec des aciers contenant du molybdène et du tungstène. Les résultats ont été satisfaisants. Le vanadium et le manganèse n'interfèrent pas. Le fer est éliminé par filtration après la fusion alcaline. Même en présence de grandes quantités de fer, on ne note pas d'interférence, c'est pourquoi la méthode sert aussi pour les analyses d'aciers. Il est évident que dans ce cas il faut substituer la fusion alcaline par l'attaque de l'échantillon d'acier avec de l'eau régale. Le résidu est repris par l'acide chlorhydrique concentré jusqu'à décomposition complète, puis la solution est rendue alcaline et on suit la méthode employée pour les minerais.

RÉSUMÉ

Une méthode rapide et simple est décrite pour la séparation et la détermination du molybdène et du tungstène. Les deux métaux sont extraits sous forme de leurs sels solubles, molybdate et tungstate de sodium au moyen d'une fusion alcaline ($Na_2CO_3 + Na_2O_2$) et ensuite séparés à l'aide d'une précipitation avec du chlorure de calcium. Les précipités de molybdate et de tungstate de calcium sont filtrés, lavés et ensuite décomposés par l'acide chlorhydrique concentré. Le molybdate de calcium passe entièrement en solution alors que le tungstate donne un précipité d'acide tungstique. En calcinant ce précipité on obtient le tri-oxyde de tungstène que l'on pèse. On en déduit la teneur en tungstène.

Le filtrat de l'acide tungstique sert pour reprécipiter le molybdate de calcium en rendant la solution alcaline et en la portant à l'ébullition. Le molybdate de calcium est filtré à l'aide d'un creuset à fond poreux et calciné. Lorsque le poids est constant, le résultat multiplié par le facteur correspondant donne la teneur en molybdène. Les résultats sont satisfaisants, la séparation et la détermination des deux métaux ne demandant pas le travail d'une journée.

SUMMARY

A rapid and simple method is described for the separation and the determination of molybdenum and tungsten. Both metals are extracted as their soluble salts, sodium molybdate and sodium tungstate, by means of an alkaline fusion ($Na_2CO_3 + Na_2O_2$), after which they are separated by precipitation with calcium chloride as reagent. The precipitates of calcium molybdate and calcium tungstate are filtered,

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washed and then decomposed by concentrated hydrochloric acid. Calcium molybdate passes completely into the filtrate while calcium tungstate leaves a precipitate of tungstic acid. By calcining this precipitate, tungstic trioxide is obtained and weighed. The tungsten content is calculated therefrom.

The filtrate from tungstic acid serves for reprecipitation of calcium molybdate on making the solution alkaline and by boiling. Calcium molybdate is filtered by means of a porcelain crucible filter and then calcined. When the weight of the calcined precipitate is constant, the molybdenum content is obtained by multiplying the weight of the precipitate by the conversion factor. Results are satisfactory, separation and determination of both metals not taking more than a day's work.

ZUSAMMENFASSUNG

Es wird eine schnelle und einfache Methode für die Trennung und Bestimmung von Molybdän und Wolfram beschrieben. Die löslichen Salze beider Metalle werden durch einen Alkaliaufschluss ($Na_2CO_3 + Na_2O_2$) erhalten, und nachher durch Ausfällung mit einer Calciumchloridlösung getrennt. Die Niederschläge von Calciummolybdat und Calciumwolframat werden filtriert, gewaschen und danach mit konzentrierter Salzsäure zersetzt. Calciummolybdat geht völlig in Lösung, Calciumwolframat gibt einen Niederschlag von Wolframsäure. Durch Glühen bekommt man Wolframtrioxyd das gewogen wird, und daraus die Wolframausbeute berechnet. Das Filtrat der Wolframsäure dient zur Wiederfällung des Calciummolybdats. Die Lösung wird alkalisch gemacht und zum Sieden gebracht. Calciummolybdat wird mit Hilfe eines Porzellanfiltertiegels filtriert und geglüht. Nach Gewichtskonstanz wird das Gewicht mit einem Faktor multipliziert um die Molybdänausbeute zuerhalten. Die Resultate sind zufriedenstellend, die Trennung und die Bestimmung beider Metalle nehmen nicht mehr als einen Tag in Anspruch.

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MANDELIC ACID AND HALOGEN-SUBSTITUTED MANDELIC ACIDS AS REAGENTS FOR THE DETERMINATION OF ZIRCONIUM

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Mandelic acid was proposed as a reagent for the gravimetric determination of zirconium by KUMINS[1], further investigations on the method being reported by HAHN[2]. These authors ignited the zirconium mandelate and weighed the precipitate as oxide. OESPER AND KLINGENBERG[3] stated that the possibility of weighing zirconium mandelate directly is slight because a high concentration of reagent is used for the precipitation and the excess cannot be removed effectively, especially since the precipitate is appreciably soluble in water. The latter authors have shown that various nuclear-substituted mandelic acids give insoluble derivatives with zirconium, and they recommended the use of the *p*-bromomandelic acid compound for the gravimetric determination of this metal[3]. Furthermore, they claimed that the precipitate formed by the bromo-acid could be weighed directly when zirconium was being determined in pure solutions and in the presence of added co-solutes; though when the direct weighing technique was applied to samples of ores and alloys the results were erratic and unreliable. Subsequently, however, KLINGENBERG AND PAPUCCI[4] have claimed that the direct weighing of zirconium *p*-bromomandelate can be applied to the determination of zirconium in steels. Meanwhile, thermogravimetric analyses of zirconium mandelate and zirconium *p*-bromomandelate carried out by STACHTCHENKO AND DUVAL[5] have indicated that the formula of the first compound approximates closely to $Zr(C_6H_5CH.OH.COO)_4$ whilst the second substance has no definite formula, although in a determination the recovery of zirconium is complete and the correct result is obtained when the precipitate is ignited to zirconium oxide.

In this paper we report the preparations of the three fluoro- and the three trifluoromethyl substituted mandelic acids, and studies upon their possible uses as precipitants for zirconium. Also, we describe investigations upon the direct weighing of zirconium mandelate and zirconium *p*-bromomandelate which were carried out in order to decide between the conflicting claims summarised above.

SYNTHESIS OF FLUORINE-CONTAINING MANDELIC ACIDS

The three isomeric fluoromandelic acids were prepared by standard procedures[6,7] which involved the bromination of the corresponding fluorotoluene to the benzal bromide, followed by hydrolysis to give the fluorobenzaldehyde, which was then converted, by addition of hydrogen cyanide followed by hydrolysis, to the fluoromandelic acid. These acids have been prepared also by HAGER AND STARKEY[8] but their products were, apparently, somewhat impure, since the analyses were outside the usual limits of experimental error and the melting points were low in comparison with our values.

o-Trifluoromethylmandelic acid was prepared from *o*-trifluoromethylbenzaldehyde by the adaptation of the procedure used by JENKINS[9] for the preparation of *p*-chloromandelic acid. *o*-Trifluoromethylbenzaldehyde was made from *o*-xylene by chlorination to give *ω*-pentachloro-*o*-xylene[10] of which the trichloromethyl group was exchanged by treatment with anhydrous hydrofluoric acid with the formation of *o*-dichloromethylbenzotrifluoride, which, in turn, was subjected to hydrolysis with sulphuric acid to give the aldehyde. The structure of the latter was confirmed by oxidation to *o*-trifluoromethylbenzoic acid.

m-Trifluoromethylmandelic acid was synthesised from *m*-trifluoromethylbenzaldehyde, which had been prepared from *m*-aminobenzotrifluoride by a modification of the process described by BROWN, SUCKLING AND WHALLEY[11].

In the preparation of *p*-trifluoromethylbenzaldehyde, which was converted to *p*-trifluoromethylmandelic acid in the normal way, the following reactions were used. *p*-Nitrotoluene was brominated, by a modification of the method used by JONES[12], to give *p*-nitrobenzotribromide, which in turn was fluorinated to *p*-nitrobenzotrifluoride and this was then reduced to the corresponding amine[12]. *p*-Aminobenzotrifluoride was converted into *p*-cyanobenzotrifluoride by a SANDMEYER reaction, and *p*-trifluoromethylbenzaldehyde was made from the cyanide in the usual way. Whilst this work was in progress the last two stages have been described, in another connection, by BERNSTEIN, YALE, LOSEE, HOLSING, MARTINS, AND LOTT[13]. The structures of our samples of *p*-trifluoromethylphenyl cyanide and -benzaldehyde were confirmed by hydrolysis and oxidation respectively to give the known *p*-trifluoromethylbenzoic acid.

ANALYTICAL PROCEDURES

Sensitivity

The six fluoro-derivatives of mandelic acid, together with α-hydroxy-α-trifluoromethylpropionic acid[14], were tested qualitatively with zirconium solutions. Only two, *p*-fluoro- and *p*-trifluoromethyl-mandelic acid were found to be of the same order of sensitivity, in the precipitation of insoluble zirconium compounds, as were mandelic acid and *p*-bromomandelic acid. In these sensitivity tests a $0.1M$

solution of each acid was added to a solution of zirconium oxychloride, of known strength, in 1.6*N* hydrochloric acid.

Precipitations obtained using *p*-fluoro- and *p*-trifluoromethyl-mandelic acid were then studied quantitatively at various concentrations of zirconium. *p*-Bromomandelic acid was also studied at lower concentrations of zirconium than those used by OESPER AND KLINGENBERG[3]. In all these analyses the zirconium was weighed as the oxide after ignition. *p*-Fluoromandelic acid was suitable for the determination of amounts of zirconium oxide as small as 6 mg, in 100 ml of solution, and 3 mg if the volume of solution was reduced to 50 ml. However, *p*-bromomandelic acid was shown to be somewhat better than *p*-fluoromandelic acid for the determination of zirconium at all concentrations since the precipitation occurred more rapidly and required a smaller excess of the organic reagent. Furthermore, *p*-bromomandelic acid precipitated the zirconium from more dilute solutions than did *p*-fluoromandelic acid. A selection of these results is given in Tables I and II. *p*-Trifluoromethylmandelic acid was also shown to be effective for the determination of amounts of zirconium oxide between 6 and 88 mg, in 100 ml of solution, but this acid is relatively difficult to prepare, and it is inferior to *p*-bromomandelic acid since the precipitate, which is often very finely divided, is formed less quickly. A selection of results is given in Table V.

Fluorine attack on crucibles

The ignition of fluorine-containing compounds in porcelain crucibles could conceivably result in attack on the crucibles by fluorine or hydrofluoric acid. Accordingly, the crucibles were ignited while containing *p*-fluoromandelic acid alone and *p*-fluoromandelic acid mixed with a known weight of zirconium oxide, and it was shown that no loss in weight occurred.

However, ignition of zirconium *p*-trifluoromethylmandelate in porcelain crucibles did have an adverse effect on the crucibles, which lost weight as a result. The recoveries of zirconium were quantitative if the precipitates were brushed out or if the ignitions were carried out in platinum crucibles.

Effect of foreign ions

A number of ions gave no precipitates with *p*-fluoro- and *p*-trifluoromethylmandelic acid in qualitative tests. The ions tested were, calcium, barium, ferric iron, uranyl, chromium, aluminium, ceric, thorium, cupric copper, manganese, cobalt, nickel, and magnesium.

As with *p*-bromomandelic acid, there is no interference with the determination if these ions are present.

Solubility of precipitates

The solubilities of the zirconium precipitates in water at 25° C were determined. The results are as follows:

Precipitate	Solubility at 25° C (g/l)
zirconium mandelate	0.1560
zirconium *p*-bromomandelate	0.0446
zirconium *p*-fluoromandelate	0.0527
zirconium *p*-trifluoromethylmandelate	0.1012

The recorded values are the average results of a series of five determinations in each case. The variability of the figures (± 0.010 g/l) may have been due to the variability in the composition of the precipitates.

Solubility of the reagents in water

A 1.0*M* solution of mandelic acid as used in these determinations is virtually a saturated solution. Similarly 0.1*M* *p*-bromomandelic acid is also very nearly a saturated solution. *p*-Fluoromandelic acid can, however, be dissolved in water to give a solution which is approximately 0.57*M*. This solution was used at low concentrations of zirconium in an attempt to precipitate the metal completely but the results given in Table I show that this was not successful.

Direct weighing of the zirconium-mandelic acid precipitates

Known weights of zirconium were precipitated from solution with *p*-bromomandelic acid and the precipitates were washed with water and dried at 110° C. The precipitates were also washed with water and then with ethanol and dried at 100° C in accordance with the procedure of KLINGENBERG AND PAPUCCI[4].

Irrespective of the method used for the washing of the precipitates the results obtained by direct weighing were low and they varied widely. However, when the precipitates were ignited to zirconium oxide the correct results were obtained (Table III).

The results are contrary to the findings of OESPER AND KLINGENBERG[3] and KLINGENBERG AND PAPUCCI[4] but are in agreement with the conclusions reported by STACHTCHENKO AND DUVAL[5].

Similar results were obtained with *p*-fluoromandelic acid. The values were low and variable (though somewhat less so than with the bromo-derivative) when the precipitates were weighed, but they were correct when the precipitates were ignited to zirconium oxide. A selection of the results is given in Table IV. Zirconium *p*-fluoromandelate has been examined by Professor DUVAL by means of his thermogravimetric balance and the curve obtained is shown in the figure.

The precipitate obtained from *p*-trifluoromethylmandelic acid also behaved in an analogous fashion, the results obtained on direct weighing being low and variable by an appreciable amount, whilst the correct values were obtained on ignition. These results are given in Table V.

Previous workers[1,2,3,4] do not report studies on the direct weighing of zirconium mandelate but STACHTCHENKO AND DUVAL[5] have stated that the formula of the precipitate approximates closely to $Zr(C_6H_5CH.OH.COO)_4$ and that the precipitate may be suitable for direct weighing.

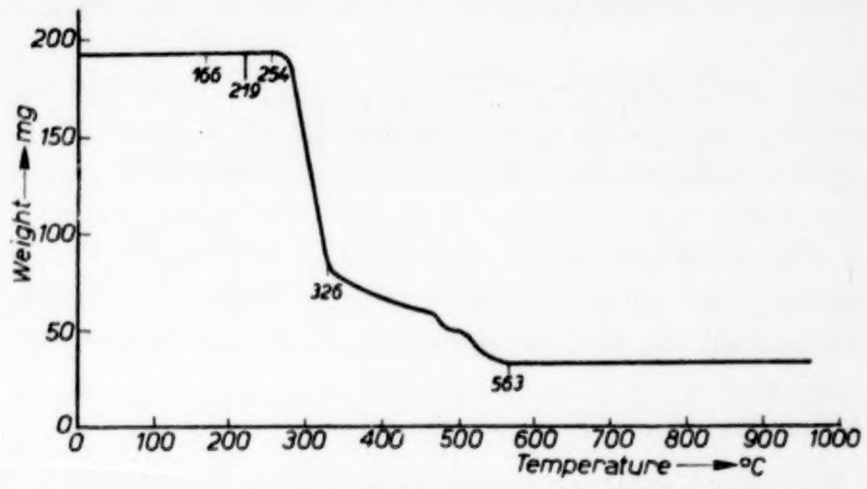

Fig. 1. Zirconium *p*-fluoromandelate.

Accordingly, we have investigated this complex in the course of the work on derivatives of mandelic acid. We found that washing of the precipitate with a solution containing 5% mandelic acid and 2% hydrochloric acid gave results which were high on direct weighing and correct on ignition, while washing with water gave low results in both cases. When the precipitate was washed with a saturated solution of zirconium mandelate itself the results, on direct weighing, were very slightly low but they were consistent. On ignition the correct values were obtained. Determinations were carried out at several different concentrations and in all cases the same effect was observed. The application of an empirical factor to the results obtained by direct weighing was considered but it was found that the empirical factor varied very slightly at different concentrations. Thus it was possible to select a factor which gave the "best fit" at all concentrations, but the results were then not as reliable as those obtained on ignition. The chosen factor was 1.0145. The results are given in Table VI (the total volume of solution in each experiment was 100 ml). Recently, ASTANINA and OSTROUMOV[18] reported that zirconium tetramandelate may be weighed directly after being washed with ethanol; they did not examine solutions having concentrations greater than 25 mg of zirconium oxide in a total volume of 100 ml. We found that the results obtained using this method were very similar to those given when the washing was carried out with saturated zirconium mandelate solution, *i.e.* at low levels the errors were comparable with the balance errors so that direct weighing gave good results, but at higher concentrations the results were low when the dried precipitate was weighed directly and correct when it was ignited.

A sample of zirconium mandelate was analysed and found to contain C, 55.0%; H, 3.8%; ZrO_2, 18.0%. The calculated values for the formula $Zr(C_6H_5CH.OH.COO)_4$ are C, 55.2%; H, 4.05%; ZrO_2, 17.7%.

A possible explanation for the non-stoichiometry of the precipitate was that it was not zirconium mandelate but some other compound such as zirconium phenylglyoxylate formed by decomposition, since the formula, $Zr(C_6H_5CO.COO)_4$, would agree closely with the results obtained by direct weighing. Accordingly, a sample of phenylglyoxylic acid was prepared[15] but it did not give a precipitate with zirconium. The zirconium-mandelic acid derivative was decomposed with ammonia solution and by extraction with ether only mandelic was recovered (yield 91%). This is very strong evidence that mandelic acid, and not some derived substance, is the organic constituent of the precipitate.

The reasons for the non-stoichiometry of the complexes of zirconium and the mandelic acids are still unknown; since the weights of the precipitates are low it appears that a small but variable proportion of the zirconium must be carried down, by co-precipitation or some similar effect, as a compound having a higher zirconium content than the tetra-mandelates of which the precipitates are largely composed.

Our findings support the work of STACHTCHENKO AND DUVAL[5] that direct weighing gives unreliable results, and in this respect are contrary to the claims of OESPER AND KLINGENBERG[3] and KLINGENBERG AND PAPUCCI[4], though the value of *p*-bromomandelic acid as a zirconium precipitant, if the complex is ignited, has been confirmed.

In addition the statement by STACHTCHENKO AND DUVAL[5] that the composition of the zirconium-mandelic acid complex corresponds closely to the formula is supported, but its non-stoichiometry makes it undesirable as a weighing form unless perhaps zirconium is to be determined in low concentrations or over narrow limits. In this case an empirical factor can be used.

TABLE I

DETERMINATIONS OF VARYING AMOUNTS OF ZIRCONIUM USING *p*-FLUOROMANDELIC ACID

Time of heating (min)	Total volume (ml)	Concentration of reagent (M)	Volume of reagent (ml)	ZrO_2 found (mg)	ZrO_2 present (mg)
40	100	0.1	50	61.2; 61.2; 61.15	61.2
20	100	0.1	50	58.7; 58.6	61.2
60	100	0.1	50	32.5; 32.4	32.4
40	100	0.1	50	31.8; 31.85	32.4
100	100	0.1	25	32.4; 32.3	32.4
60	100	0.1	25	30.8; 31.2; 30.7.	32.4
60	100	0.1	50	16.15; 16.25 16.2; 16.25	16.2
100	100	0.1	25	16.2; 16.2	16.2
60	100	0.1	50	6.4; 6.6; 6.5	6.5
60	100	0.1	25	Nil	6.5
30	50	0.2	20	6.6; 6.4	6.5
20	50	0.2	20	6.2; 5.7	6.5
20	40	0.37	10	6.6; 6.6	6.5
20	35	0.58	5	6.6; 6.6	6.5
20	40	0.58	10	3.3; 3.4	3.3
20	100	0.58	35	Nil	3.3

TABLE II

DETERMINATIONS OF VARYING AMOUNTS OF ZIRCONIUM USING *p*-BROMOMANDELIC ACID (0.1 *M*)

Time of heating (min)	Total volume (ml)	Volume of reagent (ml)	ZrO_2 found (mg)	ZrO_2 present (mg)
20	100	25	32.5; 32.5; 32.4; 32.4	32.4
20	100	25	16.2; 16.2; 16.2	16.2
20	100	12.5	15.3; 14.7; 14.9.	16.2
20	100	25	6.5; 6.5; 6.5	6.5
20	100	15	6.5; 6.4; 6.5.	6.5
20	100	10	Nil	6.5
20	100	25	3.2; 3.2	3.3
20	100	35	3.3; 3.3	3.3

TABLE III

THE DIRECT WEIGHING OF ZIRCONIUM *p*-BROMOMANDELATE (61.2 mg of ZrO_2 present)

Weight of precipitate (mg)	ZrO_2 calculated from weight of precipitate (mg)	ZrO_2 found by ignition (mg)
486.6	59.2	61.2
482.2	58.7	61.2
479.9	58.4	61.1
481.3	58.6	61.2
485.7	59.1	61.25
487.5	59.3	61.3

TABLE IV

THE DIRECT WEIGHING OF ZIRCONIUM *p*-FLUOROMANDELATE (64.0 mg of ZrO_2 present)

Weight of precipitate (mg)	ZrO_2 calculated from weight of precipitate (mg)	ZrO_2 found by ignition (mg)
394.2	63.3	63.95
392.55	63.0	64.1
393.1	63.1	63.95
390.8	62.7	63.9
391.1	62.8	64.1

TABLE V

THE DIRECT WEIGHING OF ZIRCONIUM *p*-TRIFLUOROMETHYLMANDELATE

Weight of precipitate (mg)	ZrO_2 calculated from weight of precipitate (mg)	ZrO_2 found by ignition (mg)	ZrO_2 taken (mg)
335.3	42.7	44.4	44.5
332.5	42.5	44.4	44.5
337.7	43.0	44.5	44.5
666.1	84.8	87.8	87.8
667.3	84.9	87.8	87.8
669.2	85.2	87.7	87.8
47.15	6.0	6.5	6.4
44.45	5.7	6.4	6.4

TABLE VI

THE DIRECT WEIGHING OF ZIRCONIUM MANDELATE
(after washing of the precipitate with a saturated solution of the mandelate)

Weight of precipitate (mg)	ZrO_2 calculated from weight of precipitate (mg)	Corrected ZrO_2 content. Calc. value × 1.0145 (mg)	ZrO_2 found by ignition (mg)	ZrO_2 taken (mg)
361.05	63.9	64.8	65.0	64.9
361.8	64.1	65.0	64.9	64.9
360.8	63.9	64.8	64.9	64.9
361.5	64.0	64.9	65.1	64.9
361.0	63.9	64.8	65.0	64.9
361.3	64.0	64.9	64.9	64.9
360.9	63.9	64.8	64.85	64.9
611.5	108.2	109.8	109.5	109.5
613.3	108.6	110.2	109.3	109.5
607.1	107.5	109.0	109.4	109.5
608.3	107.6	109.2	109.4	109.5
610.3	108.0	109.6	109.5	109.5
490.6	86.9	88.1	87.8	87.8
490.4	86.8	88.1	87.6	87.8
487.0	86.2	87.5	87.9	87.8
488.7	86.5	87.8	88.1	87.8
489.3	86.6	87.9	87.8	87.8
248.7	44.0	44.6	44.5	44.5
249.3	44.2	44.8	44.4	44.5
250.2	44.2	44.9	44.5	44.5
249.4	44.2	44.8	44.4	44.5
63.3	11.2	11.35	11.2	11.2
62.5	11.0	11.2	11.1	11.2
63.2	11.2	11.35	11.2	11.2
63.2	11.2	11.35	11.1	11.2
62.2	11.0	11.2	11.2	11.2
63.3	11.2	11.35	11.2	11.2

EXPERIMENTAL

Preparation of fluoromandelic acids

The fluorotoluene (75 g) was converted to the fluorobenzaldehyde by the method described for the preparation of *p*-bromobenzaldehyde[6].

The fluoromandelic acid was prepared from the fluorobenzaldehyde by the method described for the preparation of mandelic acid[7].

Isomer	Yield of aldehyde		Yield of acid		Analysis*			m.p.**
	g	%	g	%	%C	%H	%F	
Ortho	74.8	90.5	5.5	9.8	56.6	3.9	11.3	120.5° C
meta-	41.4	42.6	7.25	13.1	56.7	3.8	11.1	104° C
para-	64.7	78.0	25.4	46.2	56.5	3.9	10.9	137° C

* Calculated for $C_8H_7FO_3$; C, 56.5%; H, 4.15%; F, 11.2%.
** HAGER AND STARKEY[8] gave m.p. 116.5° C (*o*-); 101° C (*m*-); 133° C (*p*-).

*Preparation of ω-pentachloro-*o*-xylene* (with M. R. PETTIT)

o-Xylene (212 g) was placed in a two-necked round-bottomed flask fitted with a chlorine bubbler and air- and water-cooled reflux condensers. The flask was heated electrically to 120° C, the heating mantle was removed, and the flask was irradiated with ultra-violet light whilst chlorine was bubbled in slowly. Dark fumes filled the space above the liquid but when they had dispersed the chlorine flow was increased so that the temperature was maintained at 110-120° C by the heat of reaction. When the uptake of chlorine was complete the temperature fell to about 80° C, and, while the mixture was still warm, air was drawn through it to remove hydrogen chloride and excess chlorine. The product (524 g, 95%) was *ω*-pentachloro-*o*-xylene. A sample after recrystallisation from aqueous ethanol had m.p. 50° C (Found: Cl, 64.1. Calc. for $C_8H_5Cl_5$: Cl, 63.7%). SCHERER *et al.*[10] gave m.p. 48° C for this compound.

Preparation of o-*dichloromethylbenzotrifluoride* (with M. R. PETTIT)

ω-Pentachloro-*o*-xylene (278 g) and anhydrous hydrofluoric acid (180 ml) were heated together in a rocking autoclave for 12 hours at 150° C and 110-140 atmospheres pressure. The autoclave was cooled and the valve was opened to release hydrogen chloride and the excess hydrofluoric acid, the autoclave being warmed to 40° C to facilitate this process. The liquid product was transferred to a flask and distilled in steam. The distillate was extracted with ether, and the extracts were dried over magnesium sulphate and concentrated to give a liquid which, on distillation, afforded o-*dichloromethylbenzotrifluoride* (111 g, 49%), b.p. 187-189° C, n_D^{17} 1.4790 (Found: C, 42.3%; H, 1.9%; F, 24.5%. $C_8H_5Cl_2F_3$ requires C, 42.0%; H, 2.2%; F, 24.9%).

Preparation of o*-trifluoromethylbenzaldehyde*

o-Dichloromethylbenzotrifluoride (30 g) was mixed with water (10 ml) and concentrated sulphuric acid (30 ml). The mixture was stirred mechanically and heated to 100° C for 2 hours. It was then steam-distilled and the oily layer in the distillate was separated and shaken with sodium bisulphite solution. The addition compound was decomposed with dilute hydrochloric acid and the aldehyde distilled in steam. The distillate was extracted with ether, the extracts were dried over magnesium sulphate and concentrated to leave a liquid, which, on distillation, gave *o*-trifluoromethylbenzaldehyde (10 g, 44%), b.p. 64-65° C/14 mm (in the literature[16] is recorded b.p. 70° C/16 mm).

Preparation of o*-trifluoromethylbenzoic acid*

o-Trifluoromethylbenzaldehyde (1.7 g) was warmed with potassium permanganate (1.0 g) and dilute hydrochloric acid (10 ml 2*N*) on a water-bath for one hour. Sulphur dioxide was passed into the solution until it was colourless, the white solid was extracted with ether, the extracts were dried over magnesium sulphate and evaporated. The residue, on recrystallisation from water, gave *o*-trifluoromethylbenzoic acid (1.5 g, 80%), m.p. 108-109° C (Found: C, 50.3%; H, 2.5%. Calc. for $C_8H_5F_3O_2$: C, 50.55%; H, 2.65%). JONES[12] gave m.p. 107.5° C.

Preparation of o*-trifluoromethylmandelic acid*

o-Trifluoromethylbenzaldehyde (10 g) dissolved in ether (40 ml), and potassium cyanide (4.8 g) were placed in a three-necked flask which was cooled in an ice-salt bath. The contents were stirred vigorously, while concentrated hydrochloric acid (7.8 ml) was added during 15 minutes. After a further 30 minutes the ice-salt bath was removed and the stirring was continued at room temperature for 2 hours. The ethereal solution was then decanted into concentrated hydrochloric acid (50 ml) and the acid mixture was stirred and refluxed for 5 hours. The mixture was cooled, made alkaline with sodium hydroxide solution, and extracted with ether. The extracts were dried over magnesium sulphate and concentrated to leave a liquid which on distillation gave *o*-trifluoromethylbenzaldehyde (yield of recovered aldehyde 7 g, 70%). The alkaline solution was re-acidified with hydrochloric acid and extracted with ether. The extracts were dried over magnesium sulphate and evaporated. The residue, on recrystallisation from benzene, gave *o-trifluoromethylmandelic acid* (0.5 g, 13% based on the aldehyde consumed), m.p. 113-114° C (Found: C, 49.2%; H, 3.2%; F, 25.6%. $C_9H_7F_3O_3$ requires C, 49.1%; H, 3.2%; F, 25.9%).

The yield of acid was not improved by increasing the time of reaction between the aldehyde and the hydrogen cyanide.

Preparation of m-*trifluoromethylbenzaldehyde*

m-Aminobenzotrifluoride was converted to *m*-cyanobenzotrifluoride by the method of Brown, Suckling, and Whalley[11] (the product was isolated from the reaction mixture by distillation in steam, in preference to benzene extraction, and was purified by distillation). The cyanide was then converted into *m*-trifluoromethylbenzaldehyde[11], but the product was not purified after it had been isolated by steam-distillation.

Preparation of m-*trifluoromethylmandelic acid*

m-Trifluoromethylbenzaldehyde (15 g), dissolved in ether (45 ml), and potassium cyanide (6.3 g) were cooled in a flask, in an ice-salt bath, and stirred mechanically while concentrated hydrochloric acid (10 ml) was added during 30 minutes. The reaction was completed in the manner described above for the *ortho*-isomer and yielded, after recrystallisation of the product from benzene-light petroleum (b.p. 60°-80° C), m-*trifluoromethylmandelic acid* (3.75 g, 20%) m.p. 67° C (Found: C, 49.2%; H, 3.05%; F, 25.5%). This yield was low because purification was difficult; the acid separated as an intractable oil and isolation of the crystalline product was attended by serious losses.

Preparation of p-*aminobenzotrifluoride*

p-Nitrobenzotribromide was prepared from *p*-nitrotoluene by the method described by Jones[12]. It was unnecessary to decolourise the partially brominated product, and the second stage of the bromination, that using hypobromite solution, did not proceed readily in our laboratories at "room temperature". The best results were obtained at 25° C the reaction vessel being kept in a thermostatically-controlled tank. By Jones' procedures[12], *p*-nitrobenzotribromide was converted to *p*-nitrobenzotrifluoride, which was then reduced to *p*-aminobenzotrifluoride.

Preparation of p-*trifluoromethylbenzonitrile*

p-Aminobenzotrifluoride (8.05 g) was dissolved in hot hydrochloric acid (90 ml, 3*N*) and the solution was cooled rapidly in an ice-bath to 10° C and stirred vigorously. The amine was then diazotised with sodium nitrite (3.5 g) in water (9 ml). Cuprous cyanide[17] [made from copper sulphate (15 g)] and potassium cyanide (7.8 g) were dissolved in water (20 ml) and the solution was heated to 60° C and stirred while the diazonium solution was added. The mixture was refluxed for 20 minutes and steam-distilled. The distillate was filtered and the solid recrystallised from petroleum ether (b.p. 60-80° C) to give *p*-trifluoromethylbenzonitrile (3.5 g, 41%) m.p. 37-38° C (Found: C, 56.15%; H, 2.7%; F, 33.6%. Calc. for $C_8H_4F_3N$: C, 56.2%; H, 2.4%; F, 33.3%). Bernstein *et al.*[13] gave m.p. 36-37° C.

Preparation of p-*trifluoromethylbenzoic acid*

The nitrile (0.50 g) was heated at 100° C for 2 hours with concentrated hydrochloric acid (5 ml) and ethanol (1 ml). The solution was cooled, and the white solid was filtered off and sublimed to give *p*-trifluoromethylbenzoic acid (0.48 g, 87%) m.p. 218° C. JONES[12] gave m.p. 213° C.

Preparation of p-*trifluoromethylbenzaldehyde*

This aldehyde was prepared (yield 70%) from *p*-trifluoromethylbenzonitrile by the method described above for the corresponding *meta*-isomer. Oxidation as described for the *ortho*-isomer gave *p*-trifluoromethylbenzoic acid, m.p. and mixed m.p. 218° C.

Preparation of p-*trifluoromethylmandelic acid*

A mixture of *p*-trifluoromethylbenzaldehyde (7.0 g), ether (20 ml), and potassium cyanide (2.5 g) was cooled in an ice-salt bath and stirred while concentrated hydrochloric acid (4 ml) was added during 30 minutes. The reaction was completed as described above for the *ortho*-isomer, and the product, after recrystallisation from benzene, gave p-*trifluoromethylmandelic acid* (6.6 g, 75%), m.p. 129-130° C (Found: C, 49.3%; H, 3.2%; F, 25.8%).

Analytical procedure

The reagent solution was added to a solution of zirconium oxychloride, which was acidified with hydrochloric acid and was contained in a beaker. The resulting solution was heated for 20-100 minutes at 85° to 95° C and was then cooled. The precipitate was filtered off on a weighed porcelain filter crucible, and was washed and then dried for 1 hour at 105° to 115° C. The crucible was allowed to cool in the balance case for 15 minutes and then weighed. It was heated in a furnace at 900° to 950° C by the usual ignition procedure and the precipitate was converted into zirconium oxide. The crucible was allowed to cool in an empty desiccator and then in the balance case before being reweighed.

When it was unnecessary to weigh the precipitate prior to ignition, it was filtered off on a paper pulp pad, and was washed and ignited to zirconium oxide in a weighed platinum crucible.

The zirconium solutions were made up by dilution of a stock solution, the concentration of which had been determined by both the cupferron[19] and *meta*-phosphoric acid[20] precipitation methods.

Determination of solubilities

The precipitate under examination was suspended in water contained in a conical flask, immersed in a thermostatically-controlled tank, and the suspension was stirred mechanically for 48 hours. A 100 ml portion was withdrawn through a filter stick. The solution was placed in a weighed platinum dish and evaporated to dryness on a steam-bath, the dish then being reweighed.

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SUMMARY

o-, *m*-, and *p*-Fluoro- and -trifluoromethylmandelic acids have been prepared and an assessment made of their value as precipitants for zirconium. Though the *p*-derivatives are satisfactory there are no obvious advantages in their use. Direct weighings of zirconium mandelate and *p*-bromomandelate, about which there have been conflicting reports in the literature, have been investigated also. *p*-Bromomandelic acid has been used successfully for the determination of amounts of zirconium oxide between 3 and 50 mg per 100 ml but ignition of the precipitate to zirconium oxide is necessary. Of the acids examined, mandelic itself gives the only precipitate which is almost constant and stoichiometric in composition. The composition of this compound, however, varies slightly with the amount of zirconium present in the solution under test, and though an overall empirical factor can be applied its use is recommended only if a high order of accuracy is not required. If a series of determinations in a narrow range is to be carried out by direct weighing of zirconium mandelate, more accurate results might be obtained by determination of the appropriate factor for that range.

RÉSUMÉ

Les acides fluomandéliques et trifluométhylmandéliques ont été préparés et examinés comme réactifs pour la précipitation du zirconium. Bien que les acides *p*-substitués soient utilisables, ils ne présentent pas d'avantages. La pesée directe du mandélate et du *p*-bromomandélate de zirconium, sur laquelle il y a contradiction dans la littérature, a été examinée aussi. L'acide *p*-bromomandélique pour la détermination de quantités de zirconium entre 3 et 50 mg par 100 ml a été utilisé avec succès, mais il faut convertir le précipité en oxyde par ignition. L'acide mandélique est le seul de ceux que nous avons examinés qui donne un précipité dont la composition est presque constante et stoechiométrique. Néanmoins, la composition de ce composé dépend en partie de la quantité de zirconium dans la solution, et bien qu'il soit possible d'employer un facteur empirique, ce procédé est recommandé seulement quand une haute précision n'est pas nécessaire. Dans le cas où il faut faire une série de déterminations de quantités semblables par la méthode de pesée directe, il vaut mieux déterminer le facteur pour ces quantités.

ZUSAMMENFASSUNG

Die *o*-, *m*- und *p*-Fluor- und Trifluormethylmandelsäuren sind dargestellt und als Fällungsmittel für Zirkon untersucht worden. Obgleich sich die *p*-substituierten Säuren zu diesem Zweck eignen, bieten sie keinen Vorteil an. Das direkte Wiegen von Zirkonmandelat und *p*-Brommandelat, worüber Verschiedenes in der Literatur berichtet wird, ist auch untersucht worden. Mittels der *p*-Brommandelsäure gelingt es, 3 bis 50 mg pro 100 ml Zirkon zu bestimmen. Die Mandelsäure selbst ist die einzige von den untersuchten Säuren, dessen Zirkonsalz sich mit beinahe konstanter und stöchiometrischer Zusammensetzung niederschlägt. Die Zusammensetzung

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dieser Substanz kommt aber auf den Zirkongehalt der Lösung an, und ein empirischer Faktor ist nur dann zu empfehlen, wenn keine grosse Genauigkeit nötig ist. Wenn viele Bestimmungen von gleichen Mengen ohne Verbrennung durchgeführt werden sollen, ist es vorteilhaft den Faktor für diese Mengen zu bestimmen.

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QUANTITATIVE INORGANIC PAPER CHROMATOGRAPHY DIRECT DETERMINATION OF NICKEL IN MICROGRAM QUANTITIES

by

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INTRODUCTION

Although inorganic separations on filter paper have been studied by many investigators, very little work to date has been of a quantitative nature. Even then it usually involved chromatography on paper, followed by elution and analysis by some conventional analytical means *e.g.* colorimetry[1–5] or polarography[1, 6, 7]. Thus these methods are as time-consuming as standard chemical procedures, their only advantage being the possibility to work with very small quantities.

It was thought that by developing methods for the direct determination of inorganic ions on filter paper, the practical value of paper chromatography would be very much increased.

In organic paper chromatography, several methods for the direct determination of substances separated on filter paper are already available, though their accuracy is generally poor. Apart from mere visual comparison of the area and colour intensity of the spots obtained after spraying with a suitable reagent, they are based on measurement of the following properties, *cf*[8].

a. *Area of spot.* If volumes of solution of constant size are applied to the paper, the areas of the spots after chromatography are proportional to the logarithm of the concentration of material in each spot[9, 10]. The areas are determined with a planimeter, either directly on the filter paper or after photographic reproduction. This method cannot be used when there is overlapping or if the spots are distorted. With adequate replication, an accuracy of ± 5% could be obtained[11]. Different methods are used for making the spots visible, spraying with a suitable reagent being the most generally applicable. An interesting method is bioautography: substances which stimulate or inhibit microbial growth can be revealed after chromatography by the use of a microbiological indicator. The paper strips are laid on plates of a suitable medium and incubated. Zones of microbial inhibition[12] or growth[13] result, the maximum width of which is proportional to the logarithm of the concentration. A standard error of ± 15% is claimed[12].

b. *Total colour density according to* BLOCK AND BULL. Constant volumes of solutions containing known and unknown quantities of the substances under investigation are spotted on filter paper and developed one dimensionally. After colour development, the sheet is cut into strips parallel to the direction of the solvent flow and each strip is scanned at constant intervals along the length of the chromatogram using a transmission densitometer, colorimeter or spectrophotometer. The average colour densities obtained from ten or more coloured strips as well as the average absorption by the blank paper are plotted on graph paper and the areas under each peak are determined. These areas are a linear function of the concentration[14, 15]. Unless automatic scanning is used, this method is very tedious; a probable error of ± 8.8% can be expected[15].

c. *Total colour density according to* ROCKLAND. In this case the transmittancy of the entire spot is read with a densitometer or an adapted colorimeter, a suitable sample holder being used that masks all transmitted light except what passes through the coloured spot[16]. This method can only be used when the spots do not overlap and are not distorted.

d. *Maximum colour density according to* BLOCK. In this method the concentration of a substance is estimated from the minimum transmittancy of the spot, one or more standards being run on the same sheet[17]. The accuracy is only ± 10% using 18 replicate analyses. Conventional colorimeters or spectrophotometers can be used if the paper is made more transparent by impregnation with paraffin[18] or a mixture of paraffin and α-bromonaphthalene.[19]

e. *Retention analysis.* The principle of this method is the planimetric evaluation of gaps caused by the retention of parts of the solvent front by a reaction of the substance being analyzed with molecules or ions present in the solvent[20]. Thus after chromatography, a second development with the reagent solution is necessary.

f. *Automatic examination duringd evelopment.* With substances absorbing ordinary or ultraviolet light, or with fluorescent substances, the technique of MÜLLER AND CLEGG[21] can be used. Elution is conducted in a restricted channel on filter paper and its progress is followed automatically as each fraction crosses a patch of monochromatic light. A similar method using conductance measurements appears possible.

g. *Radioactivity.* On a paper chromatogram, the concentration of radioactive elements can be determined by scanning with a counting arrangement or by autoradiography [22, 23, 24, 25, 26, 27, 28].

As none of the foregoing methods appeared to be at the same time rapid, simple and accurate enough for practical inorganic analysis, a new method was developed and applied to the determination of nickel.

DEVELOPMENT OF THE METHOD

It was clear from the start that spectrophotometric measurement would provide the most precise and versatile method for direct quantitative determinations. Also that the highest accuracy would be obtained if a method could be developed along the following lines:

a) Production of initial spots in which the concentration of the unknown ion is rigorously constant all over the surface of the spot.

b) Chromatography under such conditions that all the interfering ions move away while the ion to be determined remains stationary, giving a final spot identical with the initial spot.

c) Colour development by a suitable reagent so as to obtain the highest possible sensitivity and stability.

d) Accurate measurement of the colour intensity over a constant area of the spot.

Such a method could be compared to the total colour density method of ROCKLAND, applied to non-moving spots.

In the following it will be shown how these conditions can be fulfilled in the case of the determination of nickel.

a. *Production of uniform initial spots*

1. In order that the method we contemplated should work successfully, it appeared essential to produce initial spots in which the distribution of the nickel is very uniform.

At first it seemed that this could only be achieved by the confined spot technique of YAGODA[29], which is rather tedious. When neutral or weakly acid solutions of a nickel salt are allowed to spread unchecked on filter paper, the distribution of the nickel is uneven, owing to adsorption. A ring results, the dimensions of which are dependent on the concentration of the nickel, the acid and other ions which may be present. However, we found that when strongly acid solutions ($> 1N$) are used, the nickel is distributed evenly over the entire surface of the spot. With Whatman No. 1 paper, which was used throughout, $3N$ HCl gave best results, and it was adopted for all subsequent experiments. Not only is the nickel concentration uniform throughout the spot, it is also to some extent independent of the concentration of the acid and of other ions present, all other factors remaining the same. We found that the colour intensity of the spot, after colour development, as will be described later, increases slightly with increasing concentration of the acid in the initial solution. Within the range 2.5 N — 3.5N HCl a maximum difference of 2.5% in the calculated nickel concentration was observed. This is probably due to a change in the rates of evaporation and diffusion, so that identical volumes of initial solution produce spots of a somewhat different area. For maximum accuracy it is best to keep the initial solution close to a 3N normality in HCl. Large concentrations of other ions produce a similar effect, although this may generally be neglected.

2. If the nickel is distributed evenly over the surface of the spot, it is sufficient to apply equal volumes of solution on the paper, in order to obtain always the same colour intensity for a given nickel content of the initial solution. Of course this is only true if the same type of paper is used, and if the temperature, humidity and air velocity during the application and drying of the spots remain constant. Although under ordinary circumstances the influence of atmospheric conditions is only slight, it is best always to apply a series of standards on the same chromatogram (which is necessary anyway, for other reasons which will be mentioned later). As for the paper, Whatman No. 1 was consistently used and proved satisfactory.

3. Contrary to a general rule, it is not necessary, when using our method, to keep the size of the initial spot as small as possible. Thus advantage could be taken of the full sensitivity of the photoelectric apparatus, in this case a Beckman spectrophotometer with reflectance attachment.

In this instrument the opaque mask covering the coloured sample has a circular opening 25.5 mm in diameter. To obtain maximum sensitivity the spots should be larger than this, which means that more than 0.03 ml of the initial solution must be applied to the paper. We discovered that for all practical purposes, the colour intensity per unit area is independent of the volume of the initial solution placed on the paper, within the limits 0.03-0.05 ml, all other conditions being the same. This is a distinct advantage as no accurately calibrated micropipettes are needed. Generally we applied about 0.045 ml of solution by means of an ordinary 0.2 ml micropipette graduated in 0.01 ml divisions.

After application, the paper is left at room temperature, protected from drafts, until the spots are completely dry.

Owing to the existence of a machine direction in the paper, along which diffusion is more rapid, slightly elliptical spots result, having diameters of 29-31 mm.

Summarizing, we may say that it is possible to obtain uniform initial spots, the nickel content (relative to the standard spots) per unit area of which depends only on the concentration of the nickel in the initial solution, by the very simple method of using a 3N hydrochloric acid solution and applying about 0.045 ml of this on Whatman No. 1 paper in a standardized way.

b. *Chromatography*

1. As already stated, our aim was to find a developing solvent in which the nickel would remain stationary while the interfering ions move away. Which ions interfere depends on the choice of the colour-producing reagent. For reasons given below, we used rubeanic acid, which produces coloured complexes with nickel, cobalt, copper and iron. It thus appeared necessary to find a solvent in which at least the three last elements are separated completely from the nickel. Acetone containing HCl[20] proved satisfactory, the addition of a little acetylacetone extending its usefulness. We obtained excellent results with the following mixture: acetone, 90 ml; HCl (25%), 10 ml; acetylacetone, 2 ml.

When this solvent advances through filter paper, two distinct fronts are formed: the first corresponds to the dry solvent, the second, more slowly advancing, to the wet solvent. Development is exceptionally rapid.

In this solvent, Ni moves very little ($R_F = 0.03$); Fe moves away with the first (dry) solvent front ($R_F = 1$), Cu with the second (wet) solvent front ($R_F = \pm 0.55$). Co has an R_F of about 0.45. These values were obtained under the conditions actually used for quantitative work (the filter-paper being conditioned in air at 50-65% relative humidity). No trailing is observed, except for large quantites of cobalt. Even this element however does not interfere when present in a 500 : 1 proportion.

2. For the other commonly occurring heavy metals, we found the following R_F values:

Pb: 0.75 and 0.45 (two distinct spots); Bi: 0.65; Cd: 0.6; Hg: 0.8; As: 1 and 0.55 (two distinct spots); Sb: 0.7 (very diffuse); Sn: 0.75; Al: 0.02; Cr: 0.05; Mn: 0.25; Zn: 0.75; V: 0.1; Ti: 0.7 and 0.08 (two distinct spots); MoO_4^{-2}: 0.75 (very diffuse).

It will be seen that only Al, Cr, V and Ti (the two last only partly) remain in the nickel spot, where there is a possibility of interfering with subsequent colour production.

In order to investigate the influence of large concentrations of anions which may be encountered in practical work, 2% solutions of a carbon steel were prepared. The solvent was 3*N* HCl containing about 7% of the following acids: H_2SO_4, HNO_3, $HClO_4$, H_3PO_4.

The nickel content of the steel was determined, after chromatographic development, by the usual method. When 3*N* HCl only was used, 0.21% Ni was found. With 7% H_2SO_4, HNO_3, $HClO_4$ and H_3PO_4 we found resp. 0.17%, 0.20%, 0.22% and 0.23% Ni. It follows that small amounts of nitric and perchloric acids do not interfere.

3. The chromatographic technique we use is the ascending one of WILLIAMS AND KIRBY[31] because it combines simplicity and speed and allows a large number

of chromatograms to be run at the same time. Whatman No. 1 paper sheets are cut into squares measuring 23 × 23 cm. A fine pencil line is drawn at about 5 cm from one of the sides, perpendicular to the machine direction of the paper. Six spots can be placed on this line (one blank, three standards, two unknowns). To this end, the sheet is fixed in a frame and the tip of the micropipette is brought into contact with the paper until 0.045 ml (± 0.005 ml) of solution have been absorbed. The sheet is maintained at room temperature and in air at 50-65% relative humidity and protected from draughts until the spots are completely dry (about 3/4 hour). It is then fastened together with white cotton thread in the shape of a cylinder, the edges of which must not touch. This cylinder is placed in a large glass jar containing the developing solvent to a height of about 1 cm. The jar is closed by a glass plate and the seal is made airtight by the use of desiccator grease. A large number of jars can be placed on a laboratory bench. Development is in the machine direction of the paper and takes only about 1½ hours. Elaborate temperature control is quite useless. When the (dry) solvent front reaches almost the top of the paper cylinder, the latter is removed and dried half an hour at room temperature, then half an hour between 50° and 60° C. The same solvent can be used for several runs; after three days it is discarded.

This method gives nickel spots which are only very slightly distorted in comparison to the original spots. They thus can be used for accurate reflectance measurements, as will be described under d). Fig. 1 shows a routine chromatogram (of a nickel steel sample).

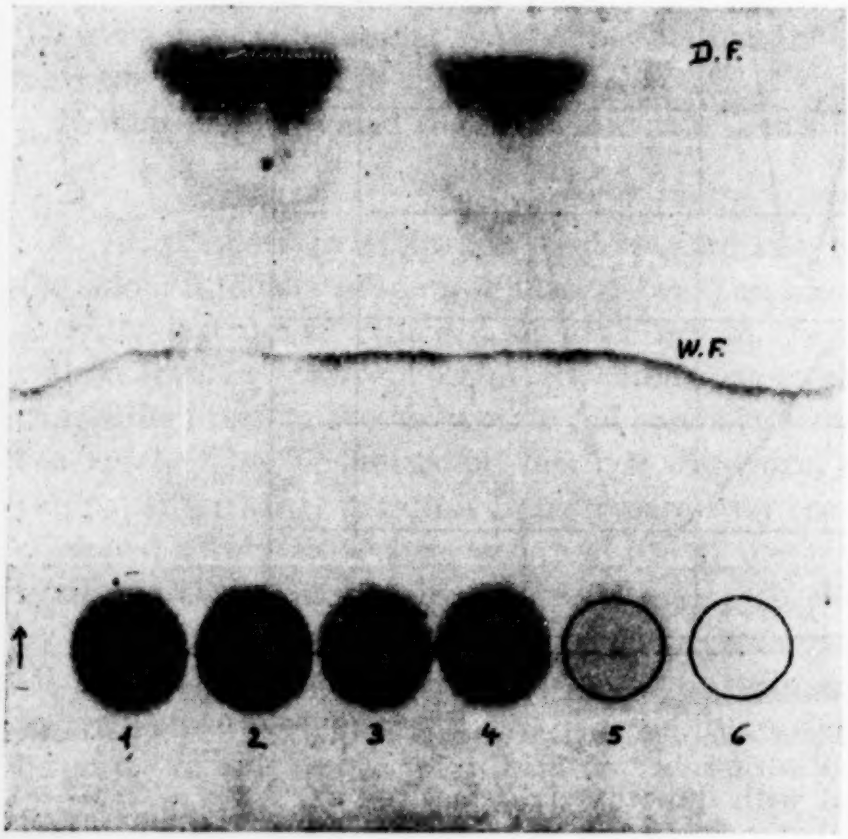

Fig 1

Chromatogram of a nickel steel.
1, 3, 5: standards.
2, 4 : unknowns.
6 : blank.
W.F. = wet solvent front.
D.F. = dry solvent front.

c. *Colour production*

1. Two reagents which produce coloured compounds with nickel ions were investigated: dimethylglyoxime and rubeanic acid (dithio-oxamide). A 0.1% solution of dimethylglyoxime and a 0.05% solution of rubeanic acid in ethanol containing 5% (vol.) of conc. ammonia were used. The addition of ammonia was found useful to prevent bleeding of the colour. These solutions are sprayed lightly and evenly on both sides of the chromatogram by means of an all-glass spray gun, with nitrogen under a pressure of 1 atm. Before spraying, any residual acidity in the filter paper is neutralized by placing the chromatogram for a few seconds in a large glass jar containing a dish filled with conc. ammonia.

Dimethylglyoxime gives a red spot, rubeanic acid a pure blue spot. The reflectance curves of spots containing equal amounts of nickel were determined on the Beckman DU spectrophotometer as described under d. Each spot was made by placing 0.045 ml of a solution containing 20 mg of Ni in 100 ml of 3N HCl on the paper; it thus contained 9 μg of Ni. Chromatographic development was carried out as usual. As the 100% standard a blank was used. Fig. 2 gives the reflectance curves in the interval 400-850 mμ, a minimum slitwidth being used throughout

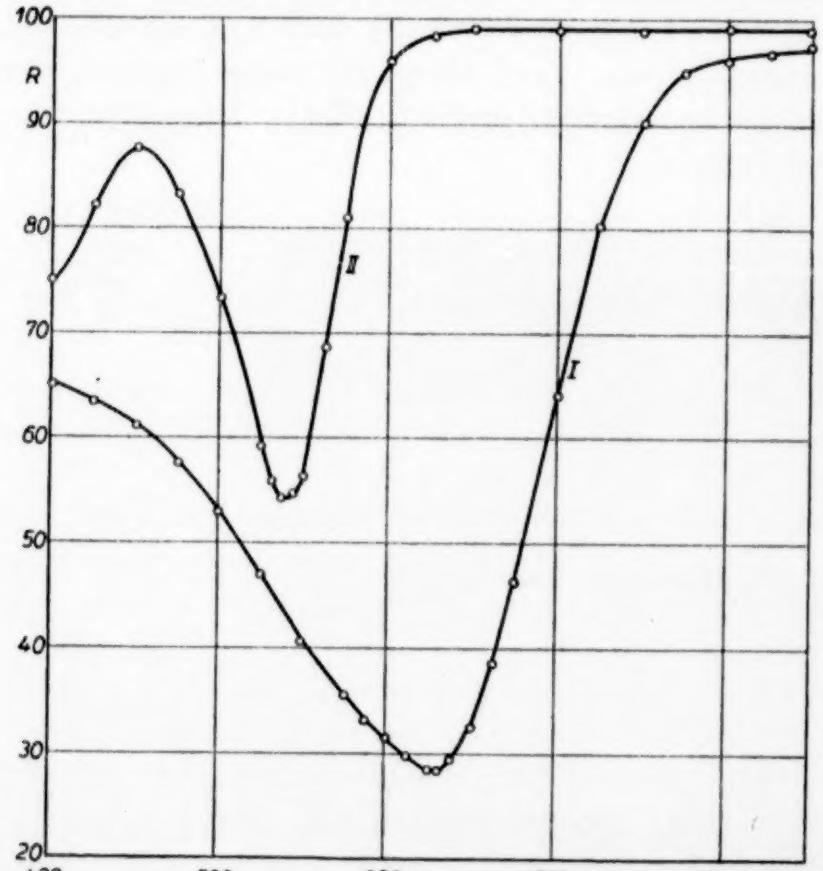

Fig. 2

Reflectance curves of identical nickel spots.

I. treated with rubeanic acid.

II. treated with dimethylglyoxime.

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The nickel-rubeanic acid spot has a minimum reflectance (28%) at 625 mμ, the nickel-dimethylglyoxime spot has a minimum reflectance (54%) at 540 mμ. This means that rubeanic acid is about 4 times more sensitive than dimethylglyoxime, and it was preferred for this reason. With this reagent quantities of nickel as low as 0.2 μg can be detected with certainty in a spot.

2. The only disadvantage of rubeanic acid is its unstability when dissolved in ammoniacal ethanol. For this reason the spraying reagent should be prepared immediately before use and discarded after half an hour. It is also necessary to run two or more standards with each chromatogram, as the reflectance values for a given nickel concentration may vary from one chromatogram to another.

The heavy metals which remain in the nickel spot, namely Al, Cr, V and Ti, although not giving a coloured compound with rubeanic acid, nevertheless interfere with the development of the nickel colour when present in large quantities (*i.e.* when their concentration is equal to or larger than that of the nickel ion). In that case low results are obtained and the direct chromatographic procedure cannot be applied. A preliminary separation of the nickel is necessary, which, owing to the small quantities involved, can very easily be achieved by extraction as the dimethylglyoxime complex with chloroform.

The colour of the nickel spots should be a pure blue: a reddish or violet colour is always an indication that large amounts of interfering metals are present, or that the spraying reagent is spoiled.

The colour of the spots is very stable if the filter paper is protected from daylight. After one month the reflectance values are 1-2% higher, but as the standards and unknowns are affected in the same way, identical results are obtained. This is a great advantage, as it is possible to carry out the measurements at any convenient time after chromatography.

It may be mentioned that rubeanic acid seems to present no health hazard[32].

d. *Colour measurement*

1. All previous investigators used transmission measurements for determining the colour intensity of spots on filter paper. This requires the use of a densitometer, a costly instrument which is of little use in the average laboratory. Ordinary colorimeters or spectrophotometers cannot, as a rule, be used, because the paper cannot be fitted in the absorption cell compartment and also because they absorb too much light. To overcome this last difficulty, it is necessary to impregnate the paper with *e.g.* paraffin. Densitometers on the other hand are generally not equipped with a monochromator and the diameter of the light beam is relatively small, so that many readings are necessary to eliminate the errors introduced by the irregularity of the filter paper. For these reasons, and because a Beckman DU spectrophotometer with reflectance attachment was available, we decided to use reflectance measurement for the quantitative evaluation of the colour intensity of the spots.

The only reference to quantitative reflectance measurements we found in the literature was the paper by WINSLOW AND LIEBHAFSKY[33]. These authors determined the directional reflectance and the transmittancy of spots containing copper treated with benzoinoxime, using a General Electric recording spectrophotometer. They concluded that transmission measurements must be preferred, because they are more sensitive and follow Beer's law, whereas reflectance measurements do not. This latter point should not be surprising, as it is well known that reflectance data for opaque materials follow the Kubelka-Munk law[34], which is quite different. As for the alleged superiority in sensitivity of transmission measurements, this is certainly true when one considers a given coloured surface[25, 35]. However, it is relatively easy to measure the reflectance of rather large surfaces; in the Beckman instrument *e.g.* the surface measured is a circle having a diameter of 25.5 mm.

A reading requires only a few seconds and monochromatic light can be used in the wavelength region 390-1000 mμ. Different measurements of the same surface never differ by more than a few tenths of 1% reflectance. By the use of a paper blank as the standard of 100% reflectance, spectrophotometric curves are obtained which compare favorably with those obtained in transmittance work. It should be noted that the Beckman instrument measures the directional reflectance $R_{0°,45°}$ with an angular spread of the reflected beam of approximately 20°. Of course any other spectrophotometer or colorimeter equipped for reflectance measurements can be used, provided the illuminated surface is smaller than the coloured spot.

2. In practice we operate as follows: on each spot a circle with a diameter of 27 mm is drawn, its centre coinciding with the approximate centre of the spot. The spot is then cut out and placed in one compartment of the drawer of the diffuse reflectance attachment while a blank spot which has been treated exactly in the same manner as the other spots is placed in the second compartment. The spots are centred under the tabs so that the circle drawn on them is invisible, the circular openings which are cut out in the tabs being slightly smaller. In this way one is always sure of measuring the central part of each spot. The wavelength dial is set at 625 mμ while the slitwidth is 0.5 mm (equivalent to an effective band width of 19 mμ). The red- or violet-sensitive phototube can be used. The spectrophotometer is adjusted to read 100% relative reflectance with the blank in measuring position. The unknown spot is then moved into the beam and its relative reflectance is read on the usual transmission scale. Filter paper is not opaque and the background must always be the same. We prefer to use a background of eight layers of Whatman No. 1 paper in both compartments. The reasons why a blank spot is used as the 100% reflectance standard, in the place of *e.g.* magnesium oxide, are the following: it is much more convenient to operate with; occasional changes in colour due to the paper or the spraying reagent are cancelled; the sensitivity is increased.

3. The readings obtained for the unknown spots are compared with those obtained for the standard spots run on the same chromatogram, and the nickel concentration of the initial solution is found by interpolation. To this end the calibration curve shown in Fig. 3 is used. It represents the average reflectance values obtained from known nickel solutions, covering the entire range from 0 to 20 mg Ni/100 ml in 1 mg/100 ml increments. To establish this curve, it was necessary to run several chromatograms, each one representing a segment of the curve. Although each individual chromatogram gives a perfectly continuous segment, two chromatograms containing the same spots may give two different but parallel segments. It is impossible to eliminate these variations, which are produced by too many uncontrollable factors. It must be emphasized that the curve of Fig. 3 is an average curve which should never be used for the direct determination of the nickel concentration in an unknown spot. For this the actual curve constructed from the standard spots run on the same chromatogram should be used. Although for a given spot the readings on the actual curve and the average curve may differ by as much as 4 units of reflectance, both curves have the same shape and are nearly parallel. By comparison with the curve

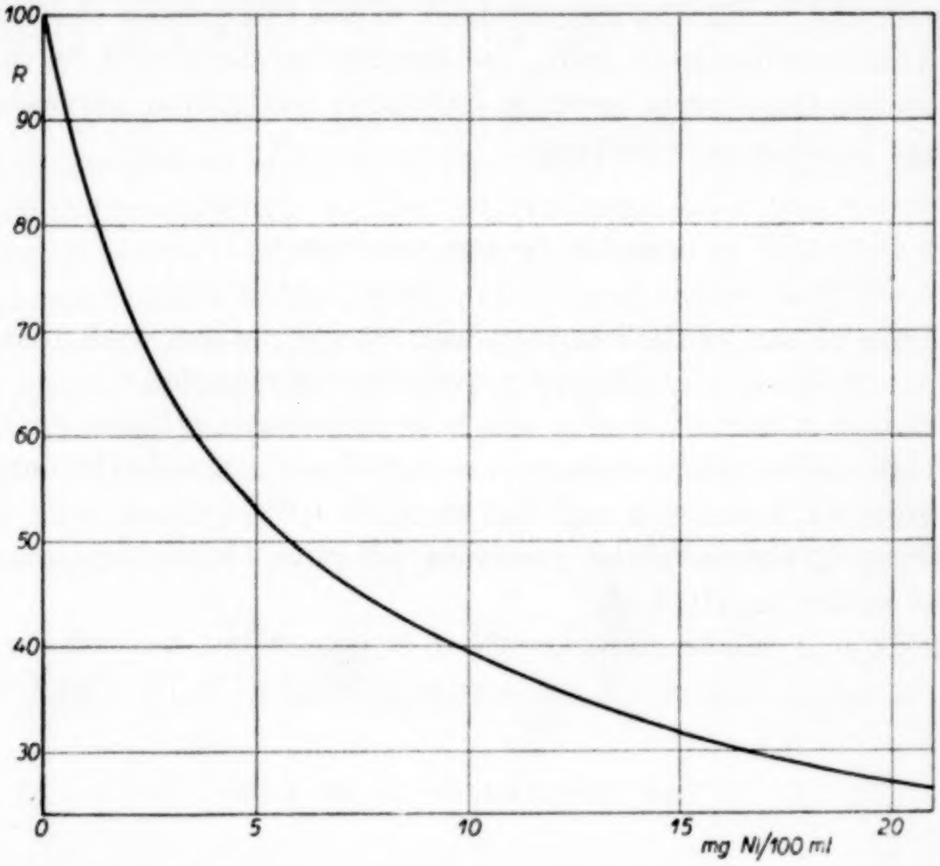

Fig. 3
Reflectance readings of spots versus Ni concentration of the initial solution. Wavelength 625 mμ.

of Fig. 3 it thus is possible to construct a complete curve from not more than 3 standard spots, corresponding to *e.g.* 3, 10 and 20 mg Ni/100 ml. From 2 standard spots a fairly large segment of the curve can be derived.

Another and better method of interpolation is to use the K/S ratio, as will be described later.

If values for the standards are obtained which differ from the curve of Fig. 3 by more than 4 reflectance units, the chromatogram should be discarded. It is our experience that, when working carefully, calibration curves rarely differ by more than 2 units of reflectance.

PRECISION AND ACCURACY

The precision of the method is very high in comparison with that attainable with other methods of quantitative paper chromatography.

The coefficient of variation of a single measurement relative to the mean is about 1.5% for concentrations from 5 to 20 mg Ni per 100 ml in the initial solution. For concentrations down to 2 mg Ni/100 ml it still is about 3%.

The accuracy is equal to the precision for pure nickel solutions and when nickel is the major constituent.

When nickel is a minor constituent, it is poorer but nevertheless compares favourably in many cases with the accuracy obtainable by chemical methods.

THE KUBELKA — MUNK LAW

As stated earlier, reflectance measurements on dyed paper should comply with the Kubelka-Munk Law:

$$R\infty = 1 + \frac{K}{S} - \left[(1 + \frac{K}{S})^2 - 1 \right]^{\frac{1}{2}}$$

where:

$R\infty$ = monochromatic reflectance of a material of such thickness that a further increase in thickness does not alter the reflectance reading.

K = absorption coefficient (fraction of incident energy lost by absorption per unit thickness of material).

S = scattering coefficient (fraction of incident energy lost due to scattering per unit thickness of material).

This can also be written: $\frac{K}{S} = \frac{(1 - R\infty)^2}{2\,R\infty}$

References p. 66/67

Within certain limits, the dye and the substratum (paper) absorb and scatter light independently of one another and the ratio K/S for the dye bears a proportionality to the amount of dye present, c [36,37]. Thus

$$kc = \left[\frac{(1-R\infty)^2}{2\,R\infty}\right] \text{total} - \left[\frac{(1-R\infty)^2}{2\,R\infty}\right] \text{paper blank.}$$

From the foregoing it can be concluded that the Kubelka-Munk law does not hold for our measurements because: a) The reflectance readings are made against a paper blank as the standard; b) The coloured material is not opaque and part of the reflectance comes from the background (8 layers of Whatman No. 1 paper have a reflectance relative to MgO of 88.0 at 625 mμ; superposing the paper blank causes a decrease of about 0.5%); c) It is not proved that the colour is distributed evenly throughout the paper at all concentrations.

Yet, when plotting the K/S values of the reflectance data of Fig. 3 against the Ni concentration, we found, much to our surprise, a linear relationship between 3 and 20 mg Ni/100 ml (Fig. 4). This means that between these limits the concentration of an unknown can easily be found by linear interpolation, the K/S

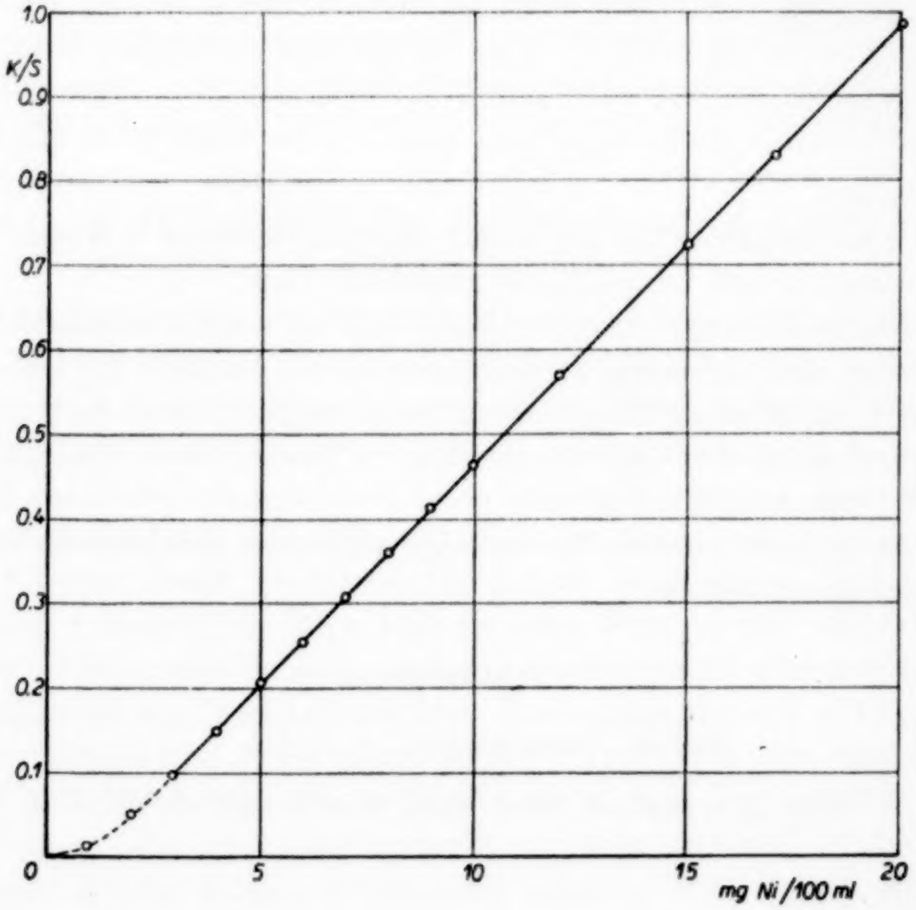

Fig. 4

K/S ratio versus Ni concentration of the initial solution. Calibration curve of Fig. 3.

line corresponding to each chromatogram having been determined from its standard spots. No calculations are needed when a K/S table [38] is available. If the K/S line is not very nearly a straight line, this means that something has gone wrong, and the chromatogram should be discarded.

APPLICATIONS

The direct method has been used successfully for the determination of nickel in the following products:

Ordinary carbon steels
Nickel steels
Cupro-nickels
Cobalt.

The lowest concentration of nickel encountered was 0.10%.

The direct method is also applicable to aluminium alloys, if the aluminium is first dissolved in NaOH.

With the addition of a preliminary extraction, the method can be used for any other material and also if the nickel content is below 0.10%.

The following alloys have been successfully analyzed:

Nickel chrome steels
Rustless steels
High-speed steels
Brasses
Aluminium alloys.

The total time required for the direct method is about 4 hours, but a large number of samples can be analyzed simultaneously.

For the preliminary extraction less than half an hour is required.

In conclusion, the following advantages can be claimed for our method: in most cases it is much faster than conventional chemical procedures; its accuracy is as good as that of the best colorimetric methods; with little difficulty very small samples can be analyzed.

Moreover it appears possible to develop analogous methods for the determination of any given cation.

EXPERIMENTAL

Direct determination of nickel

Reagents — Note: all liquids used were previously distilled in an all-glass apparatus.

$3N \pm 0.1N$ HCl

Developing solvent: 90 ml acetone + 10 ml HCl (25%) + 2 ml acetylacetone (2,4-pentanedione). Discard after 3 days.

Spraying solution: 0.05% solution of rubeanic acid (dithio-oxamide) in ethanol containing 5% (vol.) conc. ammonia. The ethanol is purified by treating it with $AgNO_3$ and KOH before distillation. The spraying solution must be prepared immediately before use and discarded after 1/2 hour.

Apparatus. Glass jars, having a diameter of about 13 cm and a height of about 25 cm. The upper edge is ground so that the jar can be closed by a glass plate and the seal made airtight with desiccator grease.
All-glass spraying gun.
Beckman spectrophotometer DU with reflectance attachment.

Procedure. A standard solution containing 0.1% Ni is prepared by dissolving a nickel salt in 3*N* HCl; the nickel content is checked by a chemical determination or by electrolysis. Solutions containing 3, 10 and 20 mg Ni in 100 ml 3*N* HCl are made from this by dilution. A solution of the unknown is prepared, containing 1-20 mg Ni/100 ml 3*N* HCl. To dissolve the sample, HCl or HNO_3 may be used. The solution is evaporated on the water bath and the residue redissolved in 3*N* HCl. Small amounts (not over 1%) of HNO_3 may remain in the final solution.

A sheet of Whatman No. 1 filter paper, measuring 23 × 23 cm, is attached in a frame. On the sheet a fine pencil line has been drawn at about 5 cm from one of the sides, perpendicular to the machine direction of the paper. On this line 6 equidistant points are marked. At each of these points a spot is formed in the following way: a micropipette (graduated in 0.01 ml divisions) which is held horizontally is brought into contact with the paper until 0.045 ± 0.005 ml of solution have been absorbed. Of the 6 spots, one is a blank (3*N* HCl), three are standards (3, 10 and 20 mg Ni/100 ml) and two are unknowns of different concentrations. Each analysis is made in duplicate.

The sheet is maintained at room temperature and at a relative air humidity of 50-65% and protected from draughts until the spots are completely dry (about 3/4 hour). It is then fastened together with white cotton thread in the shape of a cylinder, the edges of which must not touch. This cylinder is placed in a glass jar containing the developing solvent to a height of about 1 cm, and the jar is closed with a glass plate. When the solvent front nearly reaches the top of the paper cylinder (after about $1\frac{1}{2}$ hours) the latter is removed and dried half an hour at room temperature, then half an hour between 50° and 60° C. It is then placed for a few seconds in a jar containing a dish filled with conc. ammonia, in order to neutralize any residual acidity. The cotton threads are cut and the paper is again attached in a frame placed under a hood. It is then sprayed lightly and evenly on both sides with the freshly prepared spraying reagent by means of an all-glass spray gun operating under a nitrogen pressure of about 1 atm. Blue nickel spots appear at almost the same place as the original spots. After drying at room temperature, a circle having a diameter of 27 mm is drawn on each spot in such a way that its centre coincides with the centre of the spot.

The spots are cut out and their reflectance relative to the blank is measured in the Beckman DU spectrophotometer. (This may be done at any convenient time, as the colour is very stable.) To this end 8 layers of Whatman No. 1 paper are placed in each compartment of the reflectance attachment; on top of them are placed resp. the blank and the spot which must be measured. These are centred under the tabs so that the circle drawn on them is invisible.

The wavelength dial is set at 625 mμ, the slit is made as small as possible (about 0.5 mm) while still allowing a reading of 100% reflectance with the blank in measuring position. The drawer is then moved to bring the spot to be measured into the beam, and the relative reflectance is read on the usual transmission scale.

To calculate the nickel concentration of the unknown, two methods can be used. The readings obtained for the three standards may be plotted on millimeter paper against the concentration of the initial solutions, and a graph drawn with the aid of Fig. 3. The concentration of the unknown solutions can then be read from this.

Another method is to compute the K/S ratios of the standards from a K/S table and plot these on millimeter paper. A straight line can be drawn through the three points thus obtained, from which the concentration of the unknown solutions can be read.

This method cannot be used when the nickel concentration of the initial solution is below 3 mg/100 ml.

Preliminary extraction

If the nickel is accompanied by large amounts of Al, Cr, V or Ti, a preliminary extraction is necessary.

Reagents. Tartaric acid
Ammonium hydroxide, conc.
Dimethylglyoxime
Chloroform
$3N \pm 0.1N$ HCl

Procedure. The sample, containing not more than 2 mg of nickel, is dissolved in any suitable acid or mixture of acids. After dilution to about 75 ml, 2.5 g of tartaric acid are added and the solution is neutralized with conc. ammonia until distinctly alkaline. It is transferred to a 250 ml separating funnel and 0.1 g of dimethylglyoxime and 10 ml of chloroform are added. After shaking vigorously for 2 minutes, the chloroform layer is drawn off. Three more extractions are made, each with 10 ml of chloroform. If necessary, the extraction is continued until the chloroform is colourless.

The chloroform solution is shaken in a small glass-stoppered flask with exactly 10 ml of $3N$ HCl. The aqueous layer, which contains all of the nickel, can immediately be used for chromatography. A correction of 2.5% must be added to the nickel content found. For very small amounts of nickel, a correspondingly smaller volume of 3*N* HCl may be used, but the exact correction must be determined in each case.

Practical applications

Direct chromatographic procedure

Ordinary carbon steels. For ordinary carbon steels containing more than 0.10% Ni, direct chromatography can be used. A 2% solution is prepared by dissolving the sample in dilute nitric acid, evaporating on the water-bath and dissolving the residue in a suitable volume of 3*N* HCl. A 1% solution is also made by dilution. They are spotted on the filter paper to produce the two "unknown" spots.

Two British Chemical Standards* were analyzed: No. 239 (0.3% carbon steel) and No. 215 (0.9% carbon steel). Their composition, according to the certificate, was as follows: No. 239, Mn 0.73, C 0.317, Cu 0.31, Si 0.24, Ni 0.23, Cr 0.10, As 0.05, S 0.047, Sn 0.035, P 0.023, Co 0.02, Mo 0.02.

No. 215, C 0.936, Mn 0.42, Si 0.26, Ni 0.10, Cu 0.08, P 0.038, S 0.037, As 0.030, Cr 0.02, Co 0.005, Al 0.005.

Results are given in Table I.

Nickel steels. The sample is dissolved in a mixture of dilute (1:1) nitric and hydrochloric acids, the solution is evaporated and the residue is redissolved in 3*N* HCl. Two solutions, one being twice as concentrated as the other, and containing between 3 and 20 mg Ni/100 ml, are used for the "unknown" spots. We analyzed BCS No. 222 having the following composition, according to the certificate: Ni 3.39, Mn 0.7, C 0.35, Cr 0.26, Si 0.24, Cu 0.09, P 0.04, S 0.04.

Results are given in Table I.

Cupro-nickels. The sample is dissolved in dilute nitric acid, and the usua procedure is followed. We analyzed BCS No. 180 (cupro-nickel A) having the composition: Cu 68.75, Ni 30.08, Mn 0.89, Si 0.12, Fe 0.05, Mg 0.03, C 0.02, S 0.01, As 0.01, Al, Zn, Co, Pb, traces.

A belgian one franc coin was also examined. By chemical analysis, according to the usual A.S.T.M. methods, we found: Cu 74.69, Ni 24.52.

Results are given in Table I.

Cobalt. From $CoCl_2.6H_2O$ (Merck, Ni-free) and $NiSO_4. 7H_2O$ we made a synthetic sample containing 0.20% Ni for 99.80% Co. 1% and 0.5% solutions were spotted. Results are given in Table I.

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* Issued by the Bureau of Analysed Samples, Ltd., 234 Marton Road, Middlesbrough, England.

TABLE I

COMPARISON OF NICKEL DETERMINED BY THE DIRECT CHROMATOGRAPHIC METHOD AND VALUES OBTAINED BY CHEMICAL ANALYSIS

Sample	Chemical analysis		Chromatography	
	% Ni	Standard deviation (between laboratories)	% Ni	Standard deviation (between determinations)
Carbon steels				
BCS 239	0.23	0.003 (8 laboratories)	0.212	0.012 (18 detns)
BCS 215	0.10	0.014 (6 ,,)	0.106	0.002 (12 ,,)
Nickel steel				
BCS 222	3.39	0.024 (8 ,,)	3.45	0.14 (4 ,,)
Cupro-nickels				
BCS 180	30.08	0.18 (9 ,,)	30.3	0.5 (4 ,,)
Coin	24.52	—	24.5	0.4 (10 ,,)
Cobalt				
Synthetic sample	0.20	—	0.19	0.02 (4 ,,)

Extraction followed by chromatography

Nickel — chromium and chromium steels

Owing to the presence of chromium low results are generally obtained by the direct chromatographic method and a preliminary extraction is needed. The following standard samples were analyzed: BCS 225 (Ni-Cr-Mo Steel) Ni 1.67, Cr 1.04, Mn 0.595, C 0.37, Mo 0.31, Si 0.28, Cu 0.09, As 0.035, P 0.021, Sn 0.02, Co 0.01, V traces.

BCS 211 (Chromium Rustless Steel) Cr 13.80, Mn 0.34, Ni 0.33, Si 0.30, C 0.247, Mo 0.09, Cu 0.08, V 0.03, Co 0.03, P 0.017, S 0.010.

Results are given in Table II.

High speed steels

Extraction is indispensable, Cr and V interfering badly in the direct method. We analyzed the following standard samples. BCS 220: W 7.64, Cr 4.61, Mo 4.17, V 1.35, C 0.86, Co 0.67, Si 0.30, Mn 0.25, Ni 0.15, Cu 0.14.

BCS 241: W 20.28, Co 5.84, Cr 5.12, V 1.54, C 0.83, Mo 0.54, Mn 0.23, Si 0.22, Ni 0.19, Cu 0.15, Sn 0.035, S 0.035, P 0.025.

Results are given in Table II.

Manganese brass

The direct method gives slightly low results, owing to the presence of aluminium.

We used the extraction method for BCS 179 (Manganese Brass "B"):
Cu 58.8, Zn 33.9, Sn 1.75, Al 1.62, Mn 1.03, Ni 1.01, Fe 0.91, Pb 0.78, Sb 0.05, As 0.03, P 0.06.

Results are given in Table II.

Aluminium alloys

The direct method can be used if the aluminium is dissolved in a NaOH solution and the residue dissolved in $3N$ HCl. However, we preferred to use the extraction method for the analysis of BCS 216 (General Purpose Aluminium Alloy): Mn 0.73, C 0.317, Cu 0.31, Si 0.24, Ni 0.22, Cr 0.10, As 0.05, S 0.047, Sn 0.035, P 0.023, Co 0.02, Mo 0.02.

Results are given in Table II.

TABLE II

COMPARISON OF NICKEL DETERMINED BY THE CHROMATOGRAPHIC METHOD AFTER EXTRACTION AND VALUES OBTAINED BY CHEMICAL ANALYSIS

Sample	Chemical analysis		Chromatography	
	% Ni	Standard deviation (between laboratories)	% Ni	Standard deviation (between determinations)
Nickel-chromium and chromium steels				
BCS 225	1.67	0.02 (8 laboratories)	1.66	0.06 (4 detns)
BCS 211	0.33	0.018 (8 ,,)	0.324	0.008 (4 ,,)
High speed steels				
BCS 220	0.15	0.011 (11 ,,)	0.140	0.005 (4 ,,)
BCS 241	0.19	0.016 (9 ,,)	0.180	0.004 (4 ,,)
Manganese bras				
BCS 179	1.01	0.033 (10 ,,)	0.99	0.035 (4 ,,)
Aluminium alloy				
BCS 216	0.22	0.003 (9 ,,)	0.213	0.012 (4 ,,)

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SUMMARY

A method has been developed for the direct determination on filter paper of nickel, after chromatographic separation of interfering elements. The sample is dissolved in $3N$ hydrochloric acid and the solution is spotted on filter paper, together with standard solutions of nickel. After chromatographic development with a mixture of acetone, hydrochloric acid and acetylacetone, the nickel spot, which has scarcely moved, is made visible by spraying with a solution of rubeanic acid, and its reflectance is measured with a Beckman DU Spectrophotometer at 625 mμ. Most interfering elements have moved away because of their high R_F values. In the presence of large amounts ofaluminium, chromium, titanium or vanadium, a preliminary extraction of the nickel is necessary. Several technical alloys have been analyzed successfully by this method, for which only 0.045 ml of solution, containing 0.45—9 μg of nickel, are needed, although its precision is equal to that of the best colorimetric methods.

RÉSUMÉ

Une méthode a été mise au point pour la détermination directe du nickel sur papier filtre, après séparation chromatographique des autres éléments. L'échantillon est dissous dans de l'acide chlorhydrique $3N$ et la solution, de même que des solutions étalons de nickel, est appliquée sur du papier filtre de façon à former des spots uniformes. Le développement chromatographique se fait avec un mélange acétone-acide chlorhydrique-acétylacétone dans lequel le nickel est pratiquement immobile, tandis que la plupart des autres cations se déplacent sur une grande distance. Le nickel est ensuite rendu visible au moyen d'une solution d'acide rubéanique et sa réflectance est mesurée dans le spectrophotomètre Beckman DU à 625 mμ. En présence de grandes quantités d'aluminium, de chrome, de titane ou de vanadium, une extraction préliminaire du nickel s'impose. Plusieurs alliages techniquement importants ont été analysés avec succès par cette méthode, pour laquelle 0.045 ml de solution, contenant 0.45—9 μg de nickel, suffisent, et dont la précision est égale à celle des meilleures méthodes colorimétriques.

ZUSAMMENFASSUNG

Es wurde eine Methode ausgearbeitet für die direkte Bestimmung von Nickel auf Filtrierpapier nach vorhergehender chromatographischer Trennung der anderen Elementen. Die Probe wird in $3N$ Salzsäure gelöst und die Lösung, zusammen mit Standardlösungen von Nickel, wird auf Filtrierpapier aufgebracht in der Weise dass gleichmässige Flecken entstehen.

Die chromatographische Entwicklung geschieht mit einer Mischung von Aceton, Salzsäure und Acetylaceton; in dieser Lösung ist Nickel nahezu unbeweglich, während die meisten anderen Kationen weit hinwegwandern. Es wird durch eine Lösung von Rubeanwasserstoffsäure sichtbar gemacht und der Rückstrahlungswert im Beckman DU Spektrophotometer bei 625 mμ ermittelt. Bei Anwesenheit grösserer Mengen Aluminium, Chrom, Titan oder Vanadium ist eine vorhergehende Extraktion des Nickels notwendig. Der Nickelgehalt verschiedener technisch wichtigen Legierungen wurde erfolgreich bestimmt. Man braucht nur 0.045 ml Lösung, 0.45—9 μg Nickel erhaltend, doch ist die Genauigkeit gleich jener der besten kolorimetrischen Methoden.

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PRECISION DETERMINATION OF DEUTERIUM IN AQUEOUS SOLUTIONS BY A PYCNOMETER METHOD*

by

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INTRODUCTION

The mass spectrometer[1] is the instrument used for reference analysis of deuterium in aqueous mixtures. In this method, the gaseous mixture of hydrogen isotopes is ionized, separated electromagnetically, and the isotopic ratio of deuterium to hydrogen is determined by measuring the ratio of the ion currents. However, where a mass spectrometer is not available, it is desirable to have at hand other procedures which will offer precision results.

Methods for determining the percentage of deuterium oxide in aqueous solution are usually based on differential changes in physical properties: specific gravity[4,9]; refractive index[2,5]; and vapor pressure[5]. The pycnometer method for specific gravity determinations was selected for the study reported in this paper. Preliminary estimates indicated that precision results within 0.02 atom-% deuterium would be obtainable for deuterium oxide.

Neither the Geissler specific gravity bottle with thermometer insert nor the Gay-Lussac specific gravity bottle proved adequate for the work. For the present experiments, it was necessary to use the Boots specific gravity bottle (with evacuated jacket to maintain temperature, and groundglass cover to prevent evaporation). Matched pairs of bottles were selected with dry weights as close together as possible, and the double-pycnometer technique of WASHBURN AND SMITH[8] was used. The reference standards are analyzed samples of deuterium oxide and ordinary water.

EXPERIMENTAL PROCEDURE

A. *Preparation of the pycnometers*

Boots vacuum-jacketed pycnometers of 50-ml capacity were used. A water bath maintained at 25° ± 0.2 (or 30° ± 0.2) was utilized for the thermostating. Prior to use, the pycnometers were cleaned with dichromic-sulfuric acid cleaning

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* This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

solution, soaked and washed with water, rinsed with acetone, dried and stored in vacuum desiccators.

B. *High deuterium-content measurement*

Suitable volumes of the analyzed high deuterium (D)-content standard deuterium oxide, the test samples and distilled water were placed in glass stoppered volumetric flasks and thermostated at 25° C. The matched pair of calibrated specific gravity bottles was also placed in the water bath and brought to temperature. Bottle No. 1 was carefully filled from a pipette with test sample, the tip of the pipette touching the wall of the bottle to prevent formation of air bubbles. The bottle was not completely filled at this point. The bottle and contents were capped, thermostated for an additional half-hour, and the volume was then brought up to the correct level by addition of several drops of the test liquid. The bottle was taken from the thermostat and the adherent water removed from surface of the bottle by wiping with cellulose tissue. The tip of the capillary tube was not touched with the wiping pad, to avoid withdrawing an uncertain amount of liquid. The bottle was now capped and weighed.

For a determination of high deuterium oxide content, Bottle No. 2 was filled with the analyzed standard deuterium oxide in the manner described for Bottle No. 1. (If a dry box is available, fillings are preferably made inside it.)

Initial Weighings:	Bottle No. 1:	Test Solution
	Bottle No. 2:	Analyzed Standard Deuterium Oxide
Inverse Weighings:	Bottle No. 1:	Analyzed Standard Deuterium Oxide
	Bottle No. 2:	Test Solution

Initial weighings

Bottle No. 1 (test sample) was placed on the left hand pan and Bottle No. 2 (analyzed standard deuterium oxide) on the right hand pan. The difference in weight between the two was recorded (left hand weight *minus* the right hand weight). The bottles were returned to the thermostat for about one hour, then removed, dried and the weighings were repeated. At least three sets of weighings were made, and the mean value of the differences in weight was taken. This is M_1, the initial weighing.

Inverse weighings

The pycnometers were emptied, washed with water, rinsed with acetone and dried in a vacuum desiccator. Bottle No. 1 was filled with the analyzed deuterium oxide standard and Bottle No. 2 was filled with the test sample. The same technique was used, as above, with Bottle No. 1 again on the left hand pan and Bottle No. 2 on the right hand pan. This inverse weighing, M_2, is the mean value of the difference in weights, as before.

Calibration weighings

The bottles were calibrated for volume by weighing when empty and when filled with distilled water. The calibrated volume for Bottle No. 1 is 49.8352 ± 0.0016 ml and that of Bottle No. 2 is 49.8155 ± 0.0004 ml, both at 25° C. These volumes were determined with a precision of ± 0.002 ml. The calibration data are listed in Table I.

TABLE I

CALIBRATION OF VOLUME OF BOOTS PYCNOMETER

Bottle No.	Wt. of H_2O (g)	Volume (ml)	Aver. Volume (ml)	Standard Deviation (ml)
1	49.6903	49.8363	49.8352	± 0.0016
	49.6878	49.8338		
	49.6894	49.8325		
	49.6902	49.8362		
	49.6907	49.8367		
	49.6892	49.8352		
	49.6887	49.8347		
	49.6900	49.8360		
	49.6890	49.8350		
	49.6893	49.8353		
2	49.7733	49.8160	49.8155	± 0.0004
	49.7722	49.8154		
	49.7737	49.8152		

Derivations

The density may be obtained from:

$$d = \frac{M_1 - M_2}{V_1 + V_2} + d_D \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The atom-percentage of deuterium at 25° C (as derived by VOSKUYL AND DAVIS)[4,6] is given by the following, at 25° C:

$$\text{atom-\% deuterium} = \frac{927.35\ (d - d_o)}{1 - 0.0329(d - d_o)} \quad \ldots\ldots\ldots \quad (2)$$

Combining equations (1) and (2):

$$\text{atom-\% deuterium} = \frac{927.35\ \left(\dfrac{M_1 - M_2}{V_1 + V_2} + d_D - d_o\right)}{1 - 0.0329\left(\dfrac{M_1 - M_2}{V_1 + V_2} + d_D - d_o\right)} \quad \ldots\ldots\ldots\ldots \quad (3)$$

where d = density of the test solution at 25° C ± 0.2
d_o = density of distilled water at 25.00° C = 0.99707 g/ml [3]
d_D = density of the deuterium oxide, analyzed standard at 25.0° C. The density of 99.83 atom-% deuterium oxide (mass spectrometer analyzed) is 1.10434 g/ml by direct weighing. The density of pure deuterium oxide at 25.00° C is 1.10440 g/ml (1)
M_1 = initial weighing (*i.e.*, test sample in Bottle No. 1), in grams
M_2 = inverse weighing (*i.e.*, test sample in Bottle No. 2), in grams
V_1 = calibrated volume of Bottle 1, in ml
V_2 = calibrated volume of Bottle 2, in ml

The volume percentage of deuterium oxide may be of interest. It is given by the following relation(1):

$$\text{volume-\% deuterium oxide} = \frac{d - d_o}{d_{D_2O} - d_o} \quad \ldots\ldots\ldots\ldots \quad (4)$$

C. *Low deuterium-content measurement*

The procedure is analogous to that described above, but distilled water is used as the standard.

Initial Weighings: Bottle No. 1: Test Solution
Bottle No. 2: Distilled Water
Inverse Weighings: Bottle No. 1: Distilled Water
Bottle No. 2: Test Solution

The difference in density is given by:

$$d - d_o = \frac{M_1 - M_2}{V_1 + V_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Combining equations (5) and (2) yields:

$$\text{atom-\% deuterium} = \frac{927.35 \left(\dfrac{M_1' - M_2'}{V_1 + V_2}\right)}{1 - 0.0329 \left(\dfrac{M_1' - M_2'}{V_1 + V_2}\right)} \quad \ldots\ldots\ldots\ldots \quad (6)$$

The M's and the M''s are analogous.

D. *Sample calculations*

Specific examples of calculations are given below. Atom-% deuterium was calculated (a) when using analyzed deuterium oxide as standard and (b) when using distilled water as standard.

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(a)
analyzed deuterium oxide
atom-% D = 99.83

$M_1 = 0.0967$ g
$M_2 = 0.1005$ g
$V_1 = 49.8352$ ml
$V_2 = 49.8155$ ml

Substituting into equations (1) and (2):

$$d = \frac{0.0967 - 0.1005}{49.8352 + 49.8155} + 1.10434$$

$$= 1.10430 \text{ g/ml}$$

$$\text{atom-\% D} = \frac{927.35(1.10430 - 0.99707)}{1 - 0.329(1.10440 - 0.99707)}$$

$$\text{atom-\% D} = 99.79$$

Substituting into equation (4):

$$\text{vol-\% } D_2O = \frac{1.10430 - 0.99707}{1.10440 - 0.99707}$$

$$\text{vol-\% } D_2O = 99.91$$

(b)
distilled H_2O
atom-% D $\sim$ 0

$M_1' = 5.4393$ g
$M_2' = 5.2382$ g

Substituting into equations (5) and (2):

$$d - 0.99707 = \frac{5.4393 - (-5.2382)}{49.8352 + 49.8155}$$

$$d = 1.10421$$

$$\text{atom-\% D} = \frac{927.35(1.10421 - 0.99707)}{1 - 0.0329(1.10421 - 0.99707)}$$

$$\text{atom-\% D} = 99.71$$

Substituting into equation (4):

$$\text{vol-\% } D_2O = \frac{1.10421 - 0.99707}{1.10440 - 0.99707}$$

$$\text{vol-\% } D_2O = 99.82$$

RESULTS

Reproducibility

Three to five duplicate density determinations were run on twenty-two different samples. The results are given in Table II. The average standard deviation of atom-% deuterium and volume-% deuterium oxide was found to be 0.016 over the range from 1.9 to 99.9 atom-% D.

The experimental results listed in the above table were such that each set of density determinations (corresponding to a single sample) were completed within one day. To test the procedure for reproducibility over a period of time in determining density, two sets of measurements, separated by intervals of several days, were made on each of three test samples. The results are shown in Table III.

TABLE II

PRECISION DETERMINATION OF DEUTERIUM OXIDE-AQUEOUS SOLUTIONS

Sample No.	Atom-% D Average Value*	Standard Deviation	Volume-% D_2O Average Value*	Standard Deviation
1	99.885	0.013	100.001	0.016
2	99.878	0.021	99.993	0.021
3	99.855	0.011	99.971	0.012
4	99.855	0.008	99.970	0.009
5	99.780	0.006	99.895	0.006
6	99.782	0.008	99.897	0.008
7	99.517	0.010	99.633	0.011
8	98.076	0.009	98.194	0.010
9	94.109	0.024	94.237	0.024
10	88.734	0.009	88.871	0.009
11	85.409	0.016	85.552	0.016
12	60.291	0.014	60.446	0.012
13	60.279	0.017	60.433	0.015
14	59.537	0.023	59.691	0.024
15	58.451	0.028	58.604	0.028
16	53.197	0.030	53.346	0.028
17	37.199	0.010	37.324	0.009
18	16.240	0.021	16.308	0.021
19	5.905	0.019	5.932	0.021
20	4.631	0.025	4.652	0.025
21	3.131	0.023	3.138	0.025
22	1.957	0.011	1.966	0.012
	Average = 0.016		Average = 0.016	

* Three or more determinations.

TABLE III

DUPLICATION OF D_2O ANALYSES OVER TIME INTERVAL*

Sample	Standard	Atom-% D
A	Distilled H_2O	99.766 ± 0.024
		99.763 ± 0.031
B	Distilled H_2O	99.947 ± 0.017
		99.956 ± 0.028
C	99.83 atom-% D, ±0.08**	99.671 ± 0.006
		99.690 ± 0.009

* 2-3 days.

** Mass spectrometer measurement and estimated absolute precision by Argonne National Laboratory (H. T. GOODSPEED).

Precision, matched-standard method

Indication of the precision of the double-pycnometer method is shown by the results of a "matched-standard" experiment. In the matched-standard procedure, if the expected content of deuterium oxide is low, deuterium oxide in estimated

TABLE IV

DETERMINATION OF ATOM-PERCENT. DEUTERIUM USING ANALYZED DEUTERIUM OXIDE AND DISTILLED WATER AS STANDARDS

Sample No.	Distilled Water Standard Atom-% $D \sim 0$	Deuterium Oxide Standard Atom-% $D = 99.83$*
1	99.64 ± 0.02**	99.67 ± 0.01**
1a	99.62 ± 0.03**	99.69 ± 0.01**
2	99.71	99.79
3	99.72 ± 0.02	99.84 ± 0.01

* This value was determined on a mass spectrometer at Argonne National Laboratory by H. T. GOODSPEED. The absolute precision of the mass spectrometer method has been stated to be ± 0.08 atom-%. Reproducibility of determinations of a single test sample is ± 0.01 atom-%, or better.

** Samples 1 - 1a were run on successive days.

quantity is added to distilled water in order to match, or nearly match the density of the test sample. On the other hand, if the expected content of deuterium oxide is high, then distilled water is added as diluent to a high-content deuterium oxide, for matching purposes. As example, a known sample of deuterium oxide was added to 0.4372 g of distilled water, in a 500-ml volumetric flask and made up to the mark with deuterium oxide. The calculated new deuterium concentration was 99.69 atom-% D, while the pycnometer determination showed 99.67 ± 0.01 atom-% D.

TABLE V

COMPARISON OF PYCNOMETER AND MASS-SPECTROMETER ASSAYS

Sample No.	Atom-% Deuterium By Pycnometer	Atom-% Deuterium By Mass Spectrometer*
1	99.72 ± 0.01	99.746 ± 0.009
2	99.83 ± 0.01	99.839 ± 0.014
3	99.83 ± 0.02	99.890 ± 0.011
4	99.84 ± 0.02	99.829 ± 0.008

* Determinations were made at Argonne National Laboratory (H. T. GOODSPEED). The values listed represent the mean of two measurements which are different aliquots of the same sample, and the deviations shown indicate the statistical range of the two values.

In Table IV are given the results of determinations of the atom-% of deuterium in three unrelated test samples using the deuterium oxide for one set of values and the distilled water for the other set of values. Each value listed represents three to five independent weighings to determine the M's and M''s.

Additional pertinent information is summarized in Table V. The values listed in Table V are for high-content deuterium oxide samples drawn from reservoirs. The history of these samples is such that none could have a deuterium content greater than 99.84 atom-% deuterium. Each sample was carefully divided, and the deuterium concentration was determined in one portion by the double-pycnometer method with an analyzed deuterium oxide standard and in the other portion by a mass spectrometer.

DISCUSSION

As is well-known, pycnometer methods are not rapid, but they fulfil the need of a laboratory which does not have a mass spectrometer; and they provide a very desirable stand-by procedure even where a mass spectrometer is available. A standard deviation of about 0.02 atom-% deuterium is noted when 50-ml pycnometers are used, and this satisfactory number may further be diminished if 100-ml pycnometers and suitable balances are available.

Time for a complete determination (including six weighings as described) averages six hours, the major portion of which is thermostating time. Three sets of samples may conveniently be run concurrently.

In this paper, the use — as standard — of an analyzed sample of deuterium oxide which approximates the specific gravity of the test sample is described. Such a standard minimizes weighing errors, according to established principles of double-weighing with a tare, and contributes to the overall precision of the measurement. This may be called a "matched-standards" technique.

The advantage of comparing a test sample of very low atom-% deuterium (example, 2 atom-%) with distilled water as standard rather than with 99.84 atom-% deuterium is obvious. The same is true, inversely, when the test sample is 99.8 atom-% deuterium. The use of matched-standards and the double-weighing technique[8] should, in every instance offer a precision better than ± 0.04 atom-%. In case a series of standards are not conveniently obtainable, it is suggested that distilled water be used for the range of 0-25 atom-% samples, an intermediate

TABLE VI

COMPARISON OF VARIOUS STANDARDS

Sample No.	Atom-% Deuterium Found			Difference in Atom-% D		Atom-% of Intermediate Standard
	Standard = 99.83 Atom-% D	Intermediate Standard (I)	H_2O as Standard	%99.83-%I	%I-%H_2O	
1	84.59	84.64	84.45	—0.05	+0.19	59.25
2	72.32	72.26	72.29	+0.06	—0.03	27.08
3	62.55	62.49	62.37	+0.06	+0.12	5.40
4	59.28	59.23	58.92	+0.05	+0.31	84.59
5	27.25	27.14	27.08	+0.09	+0.06	72.32
6	5.51	5.43	5.40	+0.08	+0.03	62.55

standard for the 25-75 atom-% samples, and the analyzed high-content deuterium oxide standard for the 75-100 atom-% samples. Values obtained by comparing the distilled water, intermediate and high-content deuterium oxide standards with unknowns are listed in Table VI.

An important precaution in the use of deuterium oxide should be cited. To maintain its isotopic purity, deuterium oxide should be poured in a dry box. VOSKUYL AND GOREN[4,7] showed that a single pouring in air of an analyzed sample reduced the atom-% of deuterium in deuterium oxide from 99.85 to 99.83. In another example, pouring the sample back and forth ten times in air reduced the atom-% of deuterium from 99.91 to 99.79; pouring the sample back and forth in a dry box showed no change. These figures emphasize the necessity of protecting high-content deuterium oxide solutions from contact with atmospheric moisture. It is our experience that the use of analyzed deuterium oxide solution (handled in air) is limited to five independent determinations.

Some future determinations are to be made using selected organic liquids as permanent standards.

SUMMARY

Precision determination of deuterium (deuterium oxide) in aqueous mixtures were made by a pycnometer method over the range of 1 to 99 atom-% deuterium. The average deviation was ± 0.02 atom-% deuterium.

Absolute values of high-deuterium content samples are obtained by reference to a sample of high deuterium oxide content (> 99 atom-% deuterium) which has been measured by a mass spectrometer, instead of to distilled water. Matched-standards are also provided for intermediate-content (25-75 atom-%) deuterium oxide samples.

RÉSUMÉ

Des déterminations précises de deutérium (oxyde de deutérium) en mélanges aqueux ont été faites par une méthode au pycnomètre, sur une échelle de 1 à 99 atome-% de deutérium. La déviation moyenne est de 0.02 atome-% de deutérium. Des valeurs absolues pour des échantillons riches en deutérium sont obtenues par comparaison avec un échantillon riche en oxyde de deutérium (> 99 atome-% de deutérium) étalonné au moyen d'un spectromètre de masse. Des étalons sont également préparés pour des teneurs intermédiaires (25-75 atome-%).

ZUSAMMENFASSUNG

Präzisionsbestimmungen von Deuterium (Deuteriumoxyd) in wässrigen Mischungen wurden mit einer Pyknometermethode in einem Bereich von 1-99 Atom% Deuterium durchgeführt. Die durchschnittliche Abweichung betrug ± 0.02 Atom% Deuterium. Absolute Werte von Proben mit hohen Deuteriumgehalt werden erhalten durch Vergleich mit einer Probe von sehr hohen Deuteriumoxydgehalt (> 99 Atom% Deuterium), das mit einem Massenspektrographen bestimmt wurde anstelle mit destilliertem Wasser. Geeichte Vergleichslösungen wurden für Proben mit Zwischenwerten (25-75 Atom%) Deuteriumoxyd hergestellt.

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DETERMINATION OF IODINE IN MILK

by

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Essentially the same methods can be used that are in practice for iodine determinations in blood serum[1,2,3]. It is our intention to describe here briefly the modifications which must be made for reason of the special character of milk, as well as those introduced by us in order to improve the methods of iodine determination in general.

COMBUSTION

According to what is known about the inorganic nature[4] of iodine in milk and the absorptive cause[3,5] of losses of iodine during combustion, no strong alkaline solution is necessary. To 10 ml of milk in Pyrex test tubes we add only 1 ml of a solution 2% in NaOH and 1% in KNO_3. The ratio of concentrations OH/I still is 10^6, sufficient to prevent considerable absorption of iodine. On the other hand the excessive corrosion of test tubes, reported by several authors[3], is avoided. With the above quantities of milk and hydroxide two periods of several hours' combustion, in the interval of which another 1 ml of hydroxide-nitrate solution is added, are quite sufficient to give a white ash. It is our experience that remaining pieces of coal, sometimes covered with a thin white ash layer, always cause large and variable losses of iodine. For this reason we have adopted rather the criterion of a white ash endpoint than a fixed time of heating. Combustion temperature is about 550° C.

EXTRACTION

We have found that between alkaline ashing and catalytic determination no purification (distillation, extraction with organic solvents) is needed. Obviously, interfering substances[6] are either present in too low a concentration in milk to cause any trouble in the final determination or are destroyed in the ashing process. In the catalytic determination the total volume is such as to cause no precipitation of the milk calcium with sulfuric acid contained in the reagents. The ashes are extracted with several portions of warm, slightly alkaline water and filtered with small Jena glass filters in Pyrex 12 ml tubes.

PHOTOMETRY

The underlying principle is the catalytic influence[6] of iodine on the reaction between ceric sulfate and arsenious acid; the rate of disappearance of the yellow $Ce^{(IV)}$ being determined by photometry[1,2,3].

We perform two extinction readings with a 15-min interval. Procedures, with a known initial ceric sulfate concentration and one extinction reading only, have proved in our hands to suffer from interfering silica compounds. These tend to bind or to reduce some $Ce^{(IV)}$ in an instantaneous reaction, resulting in a too high iodine figure.

From the solution of the ashes only 1 ml out of 10 ml total volume is used for photometry. In this way blanks are always practically negligible, although no special oven for iodine determinations is necessary. Reaction temperature is 30° C. It must be emphasized that precautions to keep the temperature of reaction between very narrow limits are superfluous. In our measuring conditions the sensitivity of the reaction velocity to temperature changes in the region of 10° C to 50° C is exceptionally small; a difference of 1° C in temperature causing no greater effect than about 10-15%. If a Beckman type spectrophotometer (with a wavelength of 315 mμ; tungsten lamp) is used as the recording instrument, the concentration of cerium must be lowered by a factor 10, as compared with the types of photometers usually encountered in literature. The amount of iodine present is calculated from the effect of known iodine standard solutions with the following formula, derived for pseudo first order reaction kinetics.

$$\frac{I_u}{I_s} = \frac{d_u \log \text{extinction}}{d_s \log \text{extinction}},$$

(in which *u* and *s* stand for unknown and standard respectively and *d* means the difference of the logarithm of the initial and final extinction readings).

Full particulars of our method will appear in short time.

SUMMARY

A method of iodine determination in milk is described. Dry ashing and extraction of the ash with water is followed by photometric determination of the catalytic influence on the Ce-As reaction. Distillation proves to be unnecessary. Determination with this method can be performed in any laboratory, though not specially equipped for trace analyses.

RÉSUMÉ

On décrit une méthode pour la détermination de l'iode dans le lait. Elle consiste en une fusion alcaline, suivie d'une extraction des cendres à l'eau, et d'une détermination photométrique (réaction Ce-As). Une distillation est inutile. La méthode peut être utilisée dans des laboratoires, non équipés pour l'analyse des oligo-éléments.

ZUSAMMENFASSUNG

Eine Milchjodbestimmungsweise wird kurz beschrieben. Nach trockener Veraschung und Wasserextraktion der Asche folgt photometrisch die katalytische Endbestimmung. Destillieren hat sich als überflüssig nachgewiesen. Die Methode ist ohne spezielle Massnahmen in jedem Laboratorium durchzuführen.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

XVII. OXIDATION WITH CHLORAMINE-B. INDIRECT DETERMINATIONS

by

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AFANAS'EV[1] reported that chloramine-B is a good substitute for chloramine-T in analytical chemistry.

Chloramine-B reacts with potassium iodide in the presence of an acid:

$$C_6H_5SO_2N(Na)Cl + 2\ HI = C_6H_5SO_2NH_2 + NaCl + I_2.$$

In acid medium potassium iodide reacts with potassium iodate, potassium metaperiodate, potassium bromate, potassium dichromate, hydrogen peroxide, chloramine-T and potassium permanganate according to the following equations:

$$\begin{aligned}
KIO_3 + 5\ KI + 3\ H_2SO_4 &= 3\ K_2SO_4 + 3\ H_2O + 3\ I_2\\
KIO_4 + 7\ KI + 4\ H_2SO_4 &= 4\ K_2SO_4 + 4\ H_2O + 4\ I_2\\
KBrO_3 + 6\ KI + 3\ H_2SO_4 &= 3\ K_2SO_4 + KBr + 3\ H_2O + 3\ I_2\\
K_2Cr_2O_7 + 6\ KI + 7\ H_2SO_4 &= 4\ K_2SO_4 + Cr_2(SO_4)_3 + 7\ H_2O + 3\ I_2\\
H_2O_2 + 2\ KI + H_2SO_4 &= K_2SO_4 + 2\ H_2O + I_2\\
CH_3C_6H_4SO_2N(Na)Cl + 2\ HI &= CH_3C_6H_4SO_2NH_2 + NaCl + I_2\\
2\ KMnO_4 + 10\ KI + 8\ H_2SO_4 &= 6\ K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ I_2
\end{aligned}$$

The reactions have been utilised for the quantitative determination of these substances.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of potassium iodide and the mixture was acidified with $4N$ sulphuric acid. The excess potassium iodide was titrated against standard chloramine-B solution by a potentiometric method. The mixture was kept stirred by a mechanical stirrer during the titrations. A bright platinum foil immersed in the solution to be titrated was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. The cell was placed in a water bath at 25° C. During the titration the progress of the reaction was studied potentiometrically. At the equivalence point a sharp jump in potential was observed in each titration.

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A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of the set, is recorded in Table I.

TABLE I

TITRATION OF 0.1660 g OF POTASSIUM IODIDE MIXED WITH 10 ml OF WATER, 8 ml OF $4N$ H_2SO_4, AGAINST $0.052M$ CHLORAMINE-B

Chloramine-B ml	E.M.F. (volts)	E/C (m.volts/ml)
0.00	0.4051	
		10
1.00	0.4148	
		7
3.00	0.4286	
		4
5.00	0.4370	
		8
7.00	0.4538	
		14
8.00	0.4681	
		27
8.50	0.4804	
		41
9.00	0.5008	
		65
9.30	0.5204	
		154
9.50	0.5517	
		442
9.55	0.5738	
		978
9.60	0.6212	
		2330 (Maximum)
9.65	0.7377	
		754
9.70	0.7754	
		134
10.00	0.8160	
		28
10.50	0.8299	
		24
11.00	0.8421	
		14
12.00	0.8700	
		9
13.00	0.8880	
		7
15.00	0.9020	
		7
17.00	0.9160	
		6
19.00	0.9278	
		4
20.00	0.9320	

The titrations, one for each substance, are represented by the curves, A to H, given in the Fig. 1.

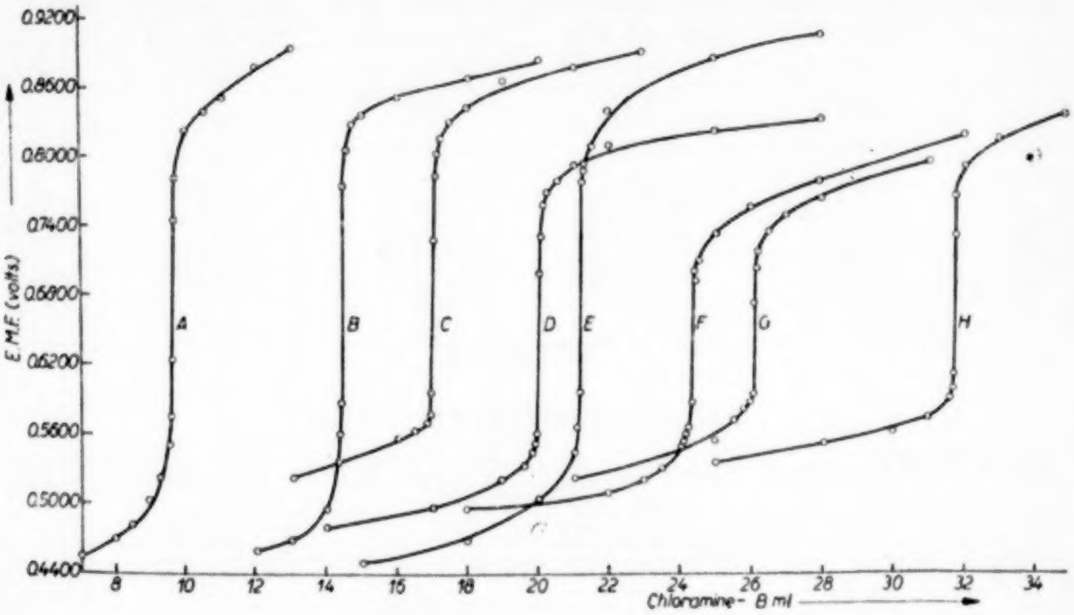

Fig. 1. Curves A-H refer respectively to KI, KIO_3, KIO_4, $KBrO_3$, $K_2Cr_2O_7$, H_2O_2, $CH_3C_6H_4SO_2N(Na)Cl$ and $KMnO_4$.

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise in each case.

From the amount of chloramine-B used, corresponding to the equivalence point in each titration, the amount of each substance was calculated. The results are given in Tables II—IX.

TABLE II

POTASSIUM IODIDE

KI taken (g)	Chloramine-B used (g)	KI found (g)
0.1660	0.1338	0.1661
0.2490	0.2008	0.2491
0.3652	0.2943	0.3653
0.4482	0.3613	0.4484
0.5478	0.4415	0.5479

TABLE III

POTASSIUM IODATE

KIO_3 taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by KIO_3	KIO_3 found
(g)	(g)	(g)	(g)	(g)	(g)
0.0299	0.2324	0.0936	0.1162	0.1162	0.0299
0.0462	0.2980	0.2007	0.2490	0.2490	0.0462
0.0941	0.7304	0.2945	0.3655	0.3649	0.0940
0.1156	0.8964	0.3614	0.4485	0.4478	0.1154
0.1413	1.0956	0.4419	0.5484	0.5471	0.1411

TABLE IV

POTASSIUM METAPERIODATE

KIO_4 taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by KIO_4	KIO_4 found
(g)	(g)	(g)	(g)	(g)	(g)
0.0230	0.2324	0.0935	0.1160	0.1164	0.0230
0.0558	0.5644	0.2273	0.2821	0.2823	0.0558
0.0722	0.7304	0.2941	0.3650	0.3654	0.0723
0.0887	0.8964	0.3610	0.4480	0.4484	0.0887
0.1084	1.0956	0.4412	0.5474	0.5482	0.1085

TABLE V

POTASSIUM BROMATE

$KBrO_3$ taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by $KBrO_3$	$KBrO_3$ found
(g)	(g)	(g)	(g)	(g)	(g)
0.0193	0.2324	0.0934	0.1160	0.1164	0.0194
0.0276	0.3320	0.1339	0.1662	0.1658	0.0276
0.0553	0.6640	0.2674	0.3318	0.3322	0.0554
0.0747	0.8964	0.3612	0.4483	0.4481	0.0747
0.0968	1.1620	0.4679	0.5807	0.5813	0.0968

TABLE VI

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by $K_2Cr_2O_7$	$K_2Cr_2O_7$ found
(g)	(g)	(g)	(g)	(g)	(g)
0.0343	0.2324	0.0936	0.1162	0.1162	0.0343
0.0735	0.4980	0.2007	0.2491	0.2489	0.0734
0.1078	0.7304	0.2943	0.3653	0.3651	0.1077
0.1323	0.8964	0.3613	0.4484	0.4480	0.1322
0.1618	1.0956	0.4415	0.5479	0.5477	0.1616

TABLE VII

HYDROGEN PEROXIDE

H_2O_2 taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by H_2O_2	H_2O_2 found
(g)	(g)	(g)	(g)	(g)	(g)
0.0168	0.3320	0.1360	0.1688	0.1632	0.0167
0.0252	0.4980	0.2035	0.2525	0.2455	0.0251
0.0369	0.7304	0.2983	0.3702	0.3602	0.0369
0.0420	0.8300	0.3398	0.4217	0.4083	0.0418
0.0453	0.8964	0.3551	0.4531	0.4433	0.0453

TABLE VIII

CHLORAMINE-T

Chloramine-T taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by Chloramine-T	Chloramine-T found
(g)	(g)	(g)	(g)	(g)	(g)
0.0976	0.2324	0.0949	0.1178	0.1146	0.0972
0.2092	0.4980	0.2032	0.2522	0.2458	0.2084
0.3068	0.7304	0.2980	0.3698	0.3606	0.3060
0.3767	0.8964	0.3643	0.4521	0.4443	0.3765
0.4604	1.0956	0.4454	0.5528	0.5428	0.4602

TABLE IX

POTASSIUM PERMANGANATE

$KMnO_4$ taken	KI added	Chloramine-B used for excess KI	Excess KI	KI used by $KMnO_4$	$KMnO_4$ found
(g)	(g)	(g)	(g)	(g)	(g)
0.0316	0.3320	0.1338	0.1661	0.1658	0.0135
0.0474	0.4980	0.2008	0.2492	0.2488	0.0473
0.0695	0.7304	0.2944	0.3653	0.3650	0.0694
0.0853	0.8964	0.3612	0.4483	0.4481	0.0852
0.1043	1.0956	0.4413	0.5477	0.5479	0.1043

The results show that potassium iodide can be determined directly and potassium iodate, potassium metaperiodate, potassium bromate, potassium dichromate, hydrogen peroxide, chloramine-T and potassium permanganate determined indirectly by the potentiometric method, using chloramine-B as an oxidising agent.

SUMMARY

Chloramine-B has been used as an oxidising agent to determine indirectly potassium iodate, potassium metaperiodate, potassium bromate, potassium dichromate, hydrogen peroxide, chloramine-T and potassium permanganate by a potentiometric method. An excess of potassium iodide added to each of the substances in an acid medium is titrated back with a standard solution of chloramine-B, using platinum foil as an oxidation-reduction electrode coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge.

RÉSUMÉ

La chloramine-B est proposée comme oxydant pour le dosage potentiométrique indirect de l'iodate, du métaperiodate, du bromate et du dichromate de potassium, du peroxyde d'hydrogène, de la chloramine-T et du permanganate de potassium. L'excès d'iodure de potassium ajouté à chacun de ces composés est titré en retour, en milieu acide, par une solution étalon de chloramine-B; on utilise une feuille de platine comme électrode d'oxydo-réduction, reliée à une électrode au calomel saturée par un pont en agar-agar-chlorure de potassium.

ZUSAMMENFASSUNG

Chloramin-B wurde bei einer potentiometrischen Methode als Oxydationsmittel zur indirekten Bestimmung von Kaliumjodat, Kaliummetaperjodat, Kaliumbromat, Kaliumdichromat, Wasserstoffsuperoxyd, Chloramin-T und Kaliumpermanganat benützt. Ein zu jeder Lösung hinzugefügter Überschuss von Kaliumjodid wird in saurer Lösung zurücktitriert mit einer Normallösung von Chloramin-B unter Benutzung einer Platinfolie als Oxydations-Reduktionselektrode, die mit einer gesättigten Kalomelektrode über eine Agar-Agar-Kaliumchloridbrücke verbunden ist.

ÉTUDE POLAROGRAPHIQUE DU MERCURE (Hg^{+2}) EN PRÉSENCE D'ACIDE ÉTHYLÈNEDIAMINOTÉTRACÉTIQUE

II. TITRAGE AMPÉROMÉTRIQUE DES CATIONS PAR LE COMPLEXON, BASÉ SUR LA VAGUE DE DÉPOLARISATION ANODIQUE

par

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Dans la première partie de ce travail[1], nous avons étudié la vague anodique de dépolarisation par le complexon et nous avons pu déterminer, à partir de la mesure du potentiel d'équilibre de la vague composée d'une solution contenant le complexe Hg^{+2}-complexon (HgY^{-2}) et un excès de complexon, la constante de stabilité de HgY^{-2}; sa valeur est égale à $10^{-22.15 \pm 0.05}$ (à 25° C, $\mu = 0.065$); nous avons montré que cette forme du complexe est la seule qui entre en ligne de compte dans le domaine de pH compris entre 4.50 et 9.25.

De plus, la constante du courant de diffusion a été trouvée invariante dans un domaine de pH allant de 4.60 à 7.49 et, possède la même valeur pour la vague de réduction du complexe mercurique et pour la vague anodique de dépolarisation; cette constante est égale à

$$I = \frac{id}{c.m^{2/3}.t^{1/6}} = 2.86 \pm 0.03 \text{ (à } 25^\circ \text{ C).}$$

Nous nous sommes proposés, dans cette note, d'examiner les possibilités d'utiliser la vague anodique du complexon pour suivre ampérométriquement le titrage de différents cations par le complexon et plus spécialement celui des alcalino-terreux.

SCHWARZENBACH et ses collaborateurs[2] ont publié une série d'articles où ils déterminent les formules et les constantes de stabilité d'un certain nombre de complexes; ces données sont rassemblées dans le Tableau I ci-dessous.

Les remarquables propriétés du complexon ont été mises à profit par PRIBIL et ses collaborateurs[3] pour les séparations analytiques de nombreux cations et d'autre part SOUCHAY ET FAUCHERRE[4] ont montré le parti que l'on pouvait en tirer en polarographie.

Conditions expérimentales

Les détails opératoires ont été décrits dans la première partie de cette publication.

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TABLEAU I

$$K_1 = \frac{[Me^{+2}].[Y^{-4}]}{[MeY^{-2}]} \qquad K_2 = \frac{[Me^{+2}].[HY^{-3}]}{[MeHY^{-2}]}$$

	K_1		K_1			K_2
Ni^{+2}	$10^{-18.45} \pm 0.07$	Co^{+2}	$10^{-16.10} \pm 0.07$	Mg^{+2}	$10^{-8.69}$	$10^{-2.28}$
Cu^{+2}	$10^{-18.38} \pm 0.07$	La^{+3}	$10^{-15.40} \pm 0.05$	Sr^{+2}	$10^{-8.63}$	$10^{-2.30}$
Pb^{+2}	$10^{-18.2} \pm 0.2$	Fe^{+2}	$10^{-14.22} \pm 0.05$	Ba^{+2}	$10^{-7.76}$	$10^{-2.07}$
Cd^{+2}	$10^{-16.47} \pm 0.05$	Mn^{+2}	$10^{-13.47} \pm 0.05$	Li^{+}	$10^{-2.785}$	
Zn^{+2}	$10^{-16.15} \pm 0.05$	Ca^{+2}	$10^{-10.69}$ et $10^{-3.51}$	Na^{+}	$10^{-1.67}$	

Des solutions tamponnées à un pH constant et contenant une concentration constante en complexon et des concentrations croissantes en cation ont été passées au polarographe; nous avons relevé, sur les polarogrammes, les valeurs des courants limites de diffusion, celles-ci nous ont permis de tracer la courbe ampérométrique.

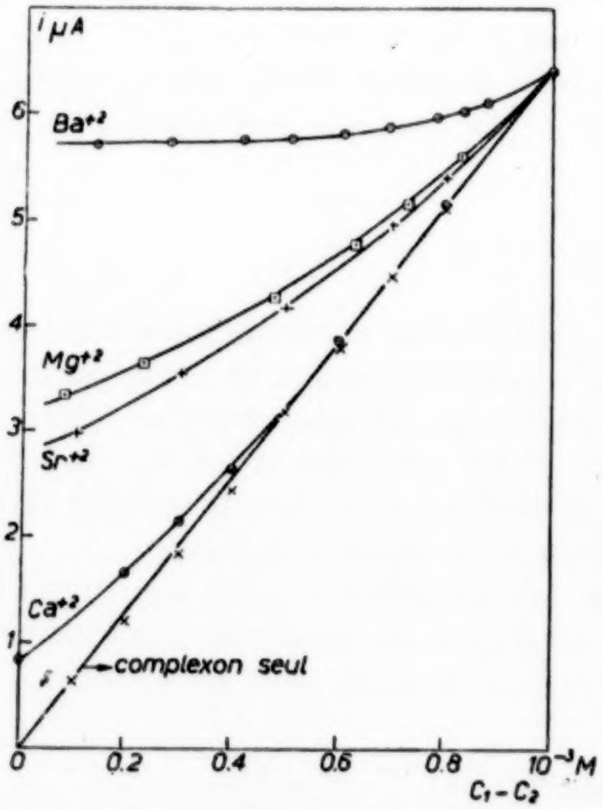

Fig. 1
Courbes ampérométriques du Ca^{+2}, Sr^{+2}, Mg^{+2}, Ba^{+2}.

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Résultats expérimentaux

1. Nous avons d'abord vérifié la validité de la loi d'Ilkovic pour la vague anodique de dépolarisation; comme le montre la Fig. 1, le courant limite de diffusion, corrigé du courant résiduel varie proportionnellement à la concentration dans le domaine étudié allant de 10^{-4} à $10^{-3} M$ (à pH = 6.4).

2. Le titrage du complexon par Mn^{+2}, Co^{+2}, Ni^{+2}, Hg^{+2}, Zn^{+2} donne au même pH de 6.4 des courbes ampérométriques normales; comme le montre le Tableau I, les complexes formés sont très stables et les courbes obtenues se superposent avec celle du complexon seul, sauf au voisinage du point équivalent.

3. Les cations alcalino-terreux, au contraire, forment des complexes moins stables et fournissent des courbes ampérométriques qui se situent très fort au

dessus de celles des autres complexes et, comme il est à prévoir, d'autant plus que le complexe est moins stable (voir Fig. 1); néanmoins il apparaît que ces écarts anormalement forts ne peuvent s'interpréter simplement sur la base de l'équilibre de dissociation du complexe.

Nous avons vu, dans la première partie de ce travail, que, dans le cas d'une solution de complexon seul, l'équilibre entre les différentes formes ionisées est constamment réalisé à l'électrode à goutte et que par conséquent la vitesse de dissociation des différentes fonctions acides est très grande vis-à-vis de la vitesse du phénomène de diffusion. On peut se demander s'il en est de même de l'équilibre de dissociation du complexe alcalino-terreux; on peut répondre immédiatement que cet équilibre n'est certainement pas réalisé à l'électrode à goutte puisque, dans ce cas, la hauteur de la vague anodique serait indépendante de la concentration en cation — ce qui n'est pas le cas —. D'autre-part, on peut examiner le cas extrême où la vitesse de dissociation du complexe serait très lente et négligeable vis-à-vis de celle du phénomène de diffusion, suivant cette hypothèse, la hauteur de la vague correspondrait à la concentration globale en complexon libre en équilibre avec le complexe au *sein de la solution*.

Nous verrons dans la discussion qui va suivre que la réalité se situe entre ces deux cas limites; il est nécessaire pour interpréter les courbes ampérométriques obtenues avec les alcalino-terreux de considérer la hauteur de la vague anodique comme la résultante de la diffusion des différentes formes du complexe libre et de la dissociation du complexe (courant cinétique), spécialement dans la couche de diffusion, s'effectuant avec une vitesse finie.

Interprétation des résultats

Vitesse de dissociation du complexe très faible

Le calcul de la courbe ampérométrique peut, dans ce cas, se faire aisément étant donné que la constante de stabilité du complexe est connue et que le milieu est tamponné.

Soit une solution de complexon dont la concentration molaire est C_1:

$$C_1 = \Theta \, . \, [\mathrm{Y}^{-4}] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\text{avec}\, \Theta = \left\{ 1 + \frac{[\mathrm{H}^+]}{K_4} + \frac{[\mathrm{H}^+]^2}{K_3.K_4} + \frac{[\mathrm{H}^+]^3}{K_2.K_3.K_4} + \frac{[\mathrm{H}^+]^4}{K_1.K_2.K_3.K_4} \right\} \quad (2)$$

Dans ces conditions, le courant limite de diffusion de la vague anodique donné par l'équation d'Ilkovic vaut:

$$i_{d\,(\mathrm{Y})} = \bar{k}_c . \Theta . [\mathrm{Y}^{-4}]\,^{*} \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

---

* $\bar{k}_c$ correspond au $\bar{k}_{\mathrm{complexon}}$ de la première partie de cet article.

Si à cette solution nous ajoutons C_2 moles de Me^{+2} nous aurons:

$$C_1 = \Theta . [Y^{-4}] + [MeY^{-2}] \quad \ldots\ldots\ldots\ldots \quad (4)$$

$$C_2 = [Me^{+2}] + [MeY^{-2}] \text{ (en négligeant } MeHY^{-}) \quad (5)$$

En combinant aux équations (5) et (6), la condition d'équilibre du complexe suivante

$$K_1 = \frac{[Me^{+2}] . [Y^{-4}]}{[MeY^{-2}]} \quad \ldots\ldots\ldots\ldots \quad (6)$$

on peut calculer la concentration en Y^{-4}:

$$Y^{-4} = -0.5 \left\{ \frac{C_1 - C_2}{\Theta} + K_1 \right\} + 0.5 \sqrt{\left\{ \frac{C_1 - C_2}{\Theta} + K_1 \right\}^2 + 4 \frac{K_1 . C_1}{\Theta}} \quad (7)$$

On obtient finalement l'équation d'Ilkovic (3) sous la forme:

$$i_{d\,(Y)} = \bar{k}_c . \Theta . \left[-0.5 \left\{ \frac{C_1 - C_2}{\Theta} + K_1 \right\} + 0.5 \sqrt{\left\{ \frac{C_1 - C_2}{\Theta} + K_1 \right\}^2 + 4 \frac{K_1 . C_1}{\Theta}} \right] \quad (8)$$

C'est l'équation théorique de la courbe ampérométrique, *dans l'hypothèse où le complexe MeY^{-2} ne participe pas à la dépolarisation anodique*, c'est-à-dire lorsqu'il possède une vitesse de dissociation très faible.

Les valeurs ainsi calculées pour Ba^{+2}, Ca^{+2}, Mg^{+2} se trouvent dans la 4ème colonne des Tableaux II, III, IV; la Fig. 2 représente les courbes ampérométriques calculées dans ces conditions.

On voit donc que les courants réels sont plus grands, il y intervient sans doute un courant supplémentaire attribuable à une décomposition du complexe avec une vitesse finie.

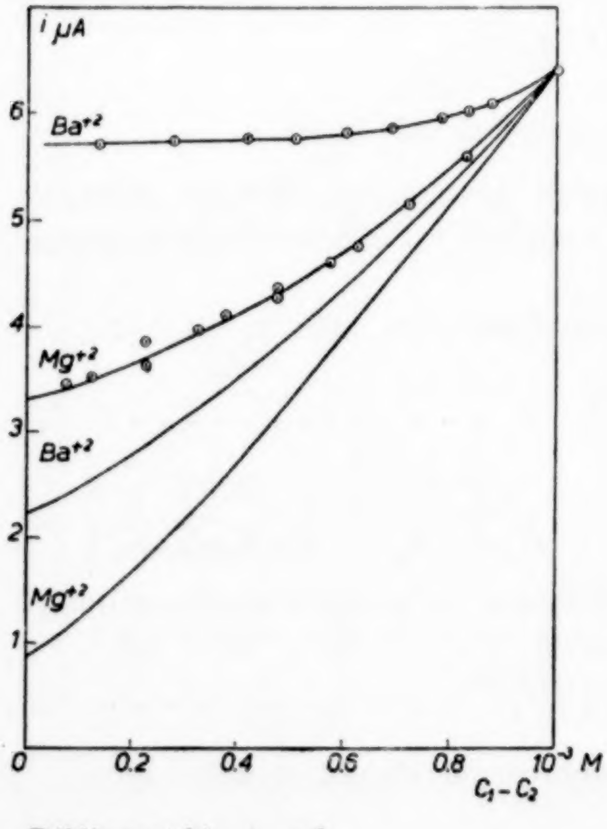

Fig. 2

Courbes ampérométriques du Ba^{+2} et Mg^{+2}

—o—o—: courbes expérimentales.

———— : courbes calculées en tenant compte de l'équilibre de dissociation des complexes avec ces deux cations.

Courant cinétique

Nous inspirant des travaux de BRDICKA[5], nous avons introduit la notion de courant cinétique, c'est-à-dire un courant additionnel dont la valeur dépend de la vitesse de décomposition de MeY^{-2}.

Nous supposons que le courant total comprend en plus du courant dû à la diffusion du complexon libre en équilibre au sein de la solution (Y^{-4}, HY^{-3}, H_2Y^{-2}, H_3Y^{-}, H_4Y) dont la concentration $\Theta.[Y^{-4}]_\circ$ dans la couche de diffusion tend vers 0, un courant cinétique i_k dû à la diffusion des ions MeY^{-2} et limité par la vitesse de dissociation.

TABLEAU II

TITRAGE AMPÉROMÉTRIQUE DU COMPLEXON PAR Ca^{+2}

pH 6.4 ± 0.1 — tampon KH_2PO_4. $0.025M$ + KOH ($\mu = 0.06$)
$t° = 25° C \pm 0.1° C$ — $E_{\text{mesure}} = 0.180^v$ vs S.C.E. (polarographe manuel)

$C_1 - C_2$ mole/litre	$[Ca^{+2}]$ ion g/litre	$\Theta.[Y^{-4}]$ ion g/litre	$i_{d_{(Y)}}$ μ amp	i_k μ amp	i_{d_t} calculé μ amp	i_{d_t} mesuré μ amp
$1.0 \cdot 10^{-3}$	0	10^{-3}	6.40	0	6.40	6.40
$0.9 \cdot 10^{-3}$	$0.6 \cdot 10^{-7}$	$0.900 \cdot 10^{-3}$	5.776	0.084	5.86	5.77
$0.8 \cdot 10^{-3}$	$1 \cdot 10^{-7}$	$0.800 \cdot 10^{-3}$	5.12	0.124	5.24	5.13
$0.7 \cdot 10^{-3}$	$1.25 \cdot 10^{-7}$	$0.700 \cdot 10^{-3}$	4.48	0.136	4.62	4.50
$0.6 \cdot 10^{-3}$	$2.2 \cdot 10^{-7}$	$0.600 \cdot 10^{-3}$	3.84	0.205	4.05	3.86
$0.5 \cdot 10^{-3}$	$3.4 \cdot 10^{-7}$	$0.500 \cdot 10^{-3}$	3.20	0.264	3.46	3.24
$0.4 \cdot 10^{-3}$	$4.6 \cdot 10^{-7}$	$0.400 \cdot 10^{-3}$	2.56	0.287	2.85	2.65
$0.3 \cdot 10^{-3}$	$6.95 \cdot 10^{-7}$	$0.300 \cdot 10^{-3}$	1.92	0.324	2.25	2.14
$0.2 \cdot 10^{-3}$	$11.7 \cdot 10^{-7}$	$0.200 \cdot 10^{-3}$	1.28	0.37	1.66	1.66
$0.1 \cdot 10^{-3}$	$25.3 \cdot 10^{-7}$	$0.102 \cdot 10^{-3}$	0.656	0.405	1.06	1.24
0	$168 \cdot 10^{-7}$	$0.0168 \cdot 10^{-3}$	0.107	0.437	0.53	0.90

Ainsi le courant total mesuré est représenté par:

$$i_{d_t} = i_{(Y)} + i_k \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

où $i_{d_{(Y)}}$ est le courant limite de diffusion théorique tiré de (8).

Rigoureusement parlant, nous devons tenir compte dans l'équation cinétique aussi bien de la vitesse de formation que de dissociation du complexe:

$$v = k_v . [MeY^{-2}]_\circ - k_v^{\bullet} . [Me^{+2}]_\circ . [Y^{-4}]_\circ \quad . . \quad (10)$$

En réalité, pour une première approximation, nous supposons que la vitesse de formation est négligeable devant celle de dissociation de sorte que nous considérons uniquement:

$$-\frac{d[MeY^{-2}]_\circ}{dt} = k_v . [MeY^{-2}]_\circ \quad \ldots\ldots\ldots \quad (11)$$

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TABLEAU III

TITRAGE AMPÉROMÉTRIQUE DU COMPLEXON PAR Mg^{+2}

pH 6.4 ± 0.1 — tampon KH_2PO_4. 0.025*M* + KOH ($\mu = 0.06$)
$t^\circ = 25.0 \pm 0.1^\circ$ C — $E_{mesure} = +0.200^v$ vs S.C.E.

$C_1 - C_2$ mole/litre	$[Mg^{+2}]$ ion g/litre	$\Theta. [Y^{-4}]$ ion g/litre	$i_{d(Y)}$ μ amp	i_k μ amp	i_d calculé μ amp	i_d mesuré μ amp
$1.0 \cdot 10^{-3}$	0	$1.0 \cdot 10^{-3}$	6.40	0	6.40	6.40
$0.9 \cdot 10^{-3}$	$2.3 \cdot 10^{-6}$	$0.902 \cdot 10^{-3}$	5.775	0.226	6.0	5.95
$0.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-6}$	$0.805 \cdot 10^{-3}$	5.15	0.422	5.57	5.50
$0.7 \cdot 10^{-3}$	$8.3 \cdot 10^{-6}$	$0.708 \cdot 10^{-3}$	4.53	0.64	5.17	5.08
$0.6 \cdot 10^{-3}$	$12.8 \cdot 10^{-6}$	$0.613 \cdot 10^{-3}$	3.92	0.86	4.78	4.70
$0.5 \cdot 10^{-3}$	$19.3 \cdot 10^{-6}$	$0.519 \cdot 10^{-3}$	3.32	1.09	4.41	4.41
$0.4 \cdot 10^{-3}$	$27.3 \cdot 10^{-6}$	$0.427 \cdot 10^{-3}$	2.74	1.28	4.02	4.12
$0.3 \cdot 10^{-3}$	$39.3 \cdot 10^{-6}$	$0.339 \cdot 10^{-3}$	2.17	1.44	3.61	3.86
$0.2 \cdot 10^{-3}$	$58.5 \cdot 10^{-6}$	$0.258 \cdot 10^{-3}$	1.65	1.65	3.31	3.65
$0.1 \cdot 10^{-3}$	$87.9 \cdot 10^{-6}$	$0.18 \cdot 10^{-3}$	1.20	1.81	3.01	3.45
0	$133.2 \cdot 10^{-6}$	$0.133 \cdot 10^{-3}$	0.85	1.937	2.79	3.30

Le courant cinétique peut être exprimé en fonction du nombre de charges électriques qui sont échangées lors de l'oxydation du mercure à l'électrode et du nombre de particules *N* qui y prennent part:

$$i_k = n.F.N \quad \dots\dots\dots\dots\dots \quad (12)$$

Pour un temps unitaire, $- \triangle\, [MeY^{-2}]_\circ = \triangle N$ (par unité de volume) (13)

Pour un volume délimité par la surface moyenne q de l'électrode à goutte et par l'épaisseur de la couche de diffusion μ, nous pouvons écrire que:

$$i_k = n.F.q.\mu.10^{-3}.\ (- \triangle [MeY^{-2}]_\circ) \quad \dots\dots \quad (14)$$

$$= n.F.q.10^{-3}.\mu.k_v.\ [MeY^{-2}]_\circ \quad \dots\dots\dots \quad (15)$$

$$\text{où } q = {}^3/_5 \,.\, 0.85 \,.\, (mt)^{2/3} \quad \dots\dots\dots\dots\dots\dots \quad (16)$$

le terme 10^{-3} est introduit parce que le volume $\mu \,.\, q$ dans lequel nous supposons que la réaction est limitée, est exprimée en ml.

D'autre-part, d'après l'équation d'Ilkovic, nous pouvons exprimer i_k sous la forme suivante:

$$i_k = k_{MeY}{}^{-2}.\ [MeY^{-2}] - [MeY^{-2}]_\circ = k_{MeY^{-2}} \,.\, [MeY^{-2}] - k_{MeY^{-2}} \,.\, [MeY^{-2}]_\circ \quad (17)$$

TABLEAU IV

TITRAGE AMPÉROMÉTRIQUE DU COMPLEXON PAR Ba^{+2}

pH = 6.4 ± 0.1 — tampon KH_2PO_4. 0.025M + KOH ($\mu = 0.06$)
$t° = 25.0°$ C ± 0.1° C — $E_{\text{mesurée}} = + 0.200^{\text{v}}$ vs. S.C.E. (pol. à lect. directe)

$C_1 - C_2$ mole/litre	$[Ba^{+2}]$ ion g/litre	$\Theta . [Y^{-4}]$ ion g/litre	$i_{d_{(Y)}}$ μ amp	i_k μ amp	i_d calculé μ amp	i_d mesuré μ amp
$1 \cdot 10^{-3}$	0	10^{-3}	6.40	0	0	6.40
$0.9 \cdot 10^{-3}$	$0.162 \cdot 10^{-4}$	$0.916 \cdot 10^{-3}$	5.86	0.397	6.26	6.13
$0.8 \cdot 10^{-3}$	$0.361 \cdot 10^{-4}$	$0.836 \cdot 10^{-3}$	5.35	0.807	6.16	5.97
$0.7 \cdot 10^{-3}$	$0.572 \cdot 10^{-4}$	$0.757 \cdot 10^{-3}$	4.85	1.16	6.01	5.86
$0.6 \cdot 10^{-3}$	$0.829 \cdot 10^{-4}$	$0.683 \cdot 10^{-3}$	4.37	1.52	5.89	5.80
$0.5 \cdot 10^{-3}$	$1.12 \cdot 10^{-4}$	$0.612 \cdot 10^{-3}$	3.92	1.84	5.76	5.76
$0.4 \cdot 10^{-3}$	$1.48 \cdot 10^{-4}$	$0.548 \cdot 10^{-3}$	3.51	2.17	5.68	5.73
$0.3 \cdot 10^{-3}$	$1.88 \cdot 10^{-4}$	$0.488 \cdot 10^{-3}$	3.12	2.45	5.56	5.72
$0.2 \cdot 10^{-3}$	$2.33 \cdot 10^{-4}$	$0.433 \cdot 10^{-3}$	2.77	2.70	5.48	5.71
$0.1 \cdot 10^{-3}$	$2.85 \cdot 10^{-4}$	$0.385 \cdot 10^{-3}$	2.47	2.94	5.41	5.70
$0.0 \cdot 10^{-3}$	$3.43 \cdot 10^{-4}$	$0.343 \cdot 10^{-3}$	2.20	3.16	5.36	5.70

d'après l'équilibre (7) nous pouvons écrire:

$$i_k = k_{\mathrm{MeY}^{-2}} \frac{[\mathrm{Me}^{+2}] \, . \, [\mathrm{Y}^{-4}]}{K_1} - k_{\mathrm{MeY}^{-2}} [\mathrm{MeY}^{-2}]_0 \quad \ldots\ldots \quad (18)$$

$$= k_{\mathrm{MeY}^{-2}} \frac{[\mathrm{Me}^{+2}] \, . \, [\mathrm{Y}^{-4}]}{K_1} - \frac{k_{\mathrm{MeY}^{-2}} . i_k . 10^3}{n.F.q.\mu.k_v} \quad \ldots\ldots \quad (19)$$

$$i_k = \frac{\mu.k_v.k_c.[\mathrm{Y}^{-4}] \, . \, [\mathrm{Me}^{+2}]}{K_1 \left\{ \mu.k_v + \dfrac{k_c . \, 10^3}{n.F.q} \right\}} \quad \ldots\ldots\ldots\ldots \quad (20)$$

En multipliant par Θ; on obtient:

$$i_k = \frac{\mu.k_v . \, i_{d_{(Y)}} \, . \, [\mathrm{Me}^{+2}]}{K_1.\Theta. \left\{ \mu.k_v + \dfrac{k_c . 10^3}{n.F.q} \right\}} \quad \ldots\ldots\ldots\ldots \quad (21)$$

où i_k et $i_{d_{(Y)}}$ sont exprimés en ampères

$\mu = 10^{-7}$ cm

m et t sont respectivement exprimés en g/sec et en secondes, $\mu.q$ en ml.

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* $k_{\mathrm{MeY}^{=}} = k_c$ au même potentiel; nous avons vu dans la première partie que la différence observée provient du terme $m^{2/3}t^{1/6}$ variant avec le potentiel auquel se fait la mesure du courant.

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Nous avons pris $k_c = 6.4 \cdot 10^{-3}$, $\Theta = 10^4$ (à pH = 6.4). Me^{+2} est la concentration exprimée en mole/l en Me^{+2} à l'équilibre au sein de la solution, c'est la concentration en ions Me^{+2} non complexés:

$$[Me^{+2}] = C_2 - [MeY^{-2}] \quad \ldots\ldots\ldots\ldots \quad (22)$$

d'après (5), nous pouvons écrire:

$$[MeY^{-2}] = C_1 - \Theta \, . \, [Y^{-4}] \quad \ldots\ldots\ldots \quad (23)$$

et finalement de ces deux dernières équations (22) et (23), nous tirons:

$$[Me^{+2}] = \Theta \, . \, [Y^{-4}] - (C_1 - C_2) \quad \ldots\ldots \quad (24)$$

L'équation de la contribution cinétique de la courbe ampérométrique (23) contient comme terme inconnu μk_v: nous pouvons le déterminer à partir d'un point de la courbe expérimentale c'est-à-dire à partir de l'équation suivante:

$$\mu . k_v = \frac{K_1 . \, \Theta \, . \, i_k}{i_{d_{(Y)}} \, . \, [Me^{+2}] - K_1 . \Theta . i_k} \cdot \frac{k_c \, . \, 10^3}{n . F . q} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (27)$$

Nous avons ainsi calculé $\mu . k_v$ et déduit de cette valeur la constante de vitesse pour les cations étudiés:

	Ca^{+2}	Mg^{+2}	Ba^{+2}
K_1	$2.56 \cdot 10^{-11}$	$2.02 \cdot 10^{-9}$	$1.74 \cdot 10^{-8}$
$\mu . k_v$	$0.9 \cdot 10^{-5}$	$7.8 \cdot 10^{-5}$	$4.3 \cdot 10^{-3}$
k_v	$0.9 \cdot 10^{2}$	$7.8 \cdot 10^{3}$	$4.3 \cdot 10^{4}$

Les valeurs de $\mu . k_v$ ont été obtenues au moyen des données expérimentales de i_{dt}, relevées dans les Tableaux I, III et IV aux valeurs de $C_1 - C_2$ suivantes:

$0.2 \cdot 10^{-3} M$ pour les ions Ca^{+2}.
$0.5 \cdot 10^{-3} M$ pour les ions Mg^{+2}.
$0.5 \cdot 10^{-3} M$ pour les ions Ba^{+2}.

Les valeurs du courant total calculées à partir de (21) sont consignées dans l'avant dernière colonne des Tableaux II, III, IV et ont servi à tracer les courbes

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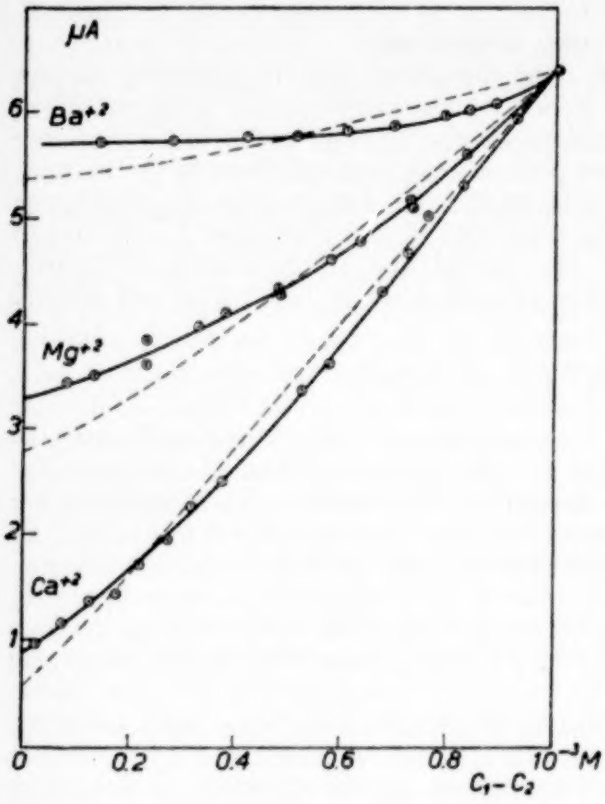

Fig. 3
Courbes ampérométriques du Ca^{+2}, Mg^{+2}, Ba^{+2}
—●—: courbes expérimentales.
- - - -: courbes calculées à partir de l'équation (9).

de la figure 3; la concordance avec les courbes expérimentales est satisfaisante.

Il semble donc que l'interprétation des courbes ampérométriques à partir du courant cinétique soit correcte.

DELAHAY[6] a également établi une équation plus rigoureuse du courant limite de diffusion lorsque le phénomène est contrôlé à la fois par la vitesse de réaction et par la diffusion; il a établi cette équation dans le cas particulier de la réduction d'une substance R formée par la réaction B→R lorsque R est négligeable devant B.

Les équations et les conclusions de cette étude peuvent s'appliquer au Ca^{+2} lorsque $C_1 - C_2 = 0$; en effet, dans ce cas, (voir Tableau II) la dissociation du complexe est pratiquement négligeable et le courant limite mesuré est d'origine cinétique seulement. Il nous a paru intéressant, dans ces conditions, de calculer la constante de vitesse k_v par la méthode graphique donnée par DELAHAY; en utilisant les valeurs suivantes:

$D = 5.5 \cdot 10^{-6}$ cm²/sec $\quad C = 10^{-3}$mole/litre, $n = 2$
$m = 2.53$ mg/sec $\quad \delta = 1.2 \cdot 10^{-6}$ cm
$t = 2.86$ sec $\quad i = 0.8$ μA

nous trouvons que $k_v = 1.2 \cdot 10^2$ sec^{-1}.

Cette valeur concorde de façon satisfaisante avec celle trouvée plus haut, à partir de la formule de BRDICKA.

Il ne faut cependant pas perdre de vue que ces valeurs trouvées pour la constante de vitesse de dissociation du complexe n'ont qu'une signification toute relative.

RÉSUMÉ

La vague anodique de dépolarisation du Hg^{+2} par le complexon (acide éthylènediaminetétracétique) a été trouvée proportionnelle à la concentration en complexon (10^{-4} à 10^{-3} mole/litre, pH = 6.4 milieu tamponné).

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Le titrage du complexon par Mn^{+2}, Co^{+2}, Ni^{+2}, Cd^{+2}, Hg^{+2}, Zn^{+2} donne, au même pH 6.4, des courbes ampérométriques normales.

Les cations alcalino-terreux, au contraire, qui forment des complexes moins stables que les précédents, fournissent des courbes ampérométriques anormales en ce sens que la hauteur de la vague observée au cours du titrage est très supérieure à celle qui correspond à la concentration du complexon non engagé dans le complexe. Ces derniers résultats se laissent néanmoins interpréter de façon très satisfaisante si l'on admet que le courant limite mesuré est contrôlé d'une part par la diffusion et d'autre part par la vitesse de dissociation des complexes au voisinage de l'électrode. La constante de vitesse est d'autant plus grande que le complexe est moins stable.

SUMMARY

The anodic depolarization wave of Hg^{+2} by complexone (ethylenediaminotetraacetic acid) has been found to be proportional to the concentration of complexone (10^{-4} to 10^{-3} mole/liter, pH = 6.4 in buffered medium). Titratione of complexone by Mn^{+2}, Co^{+2}, Ni^{+2}, Cd^{+2}, Mg^{+2}, Zn^{+2} gave, at the same pH of 6.4, normal amperometric curves. On the other hand, alkaline-earth cations, the complexes of which are less stable than the aforementioned ones, gave abnormal amperometric curves in that the height of the wave observed during titration is much larger than the one corresponding to the concentration of the complexone that is not involved in the formation of the complex.

These results can nevertheless be interpreted in a satisfactory way by assuming that the measured current is determined on the one hand by diffusion and on the other hand by the rate of dissociation of the complexes in the vicinity of the electrode. The rate constant is greater the less stable the complex.

ZUSAMMENFASSUNG

Die Depolarisierungswelle von Hg^{+2} durch das Komplexon (Aethylendiaminotetraessigsäure) wurde verhältnismässig zu der Konzentration des Komplexons (10^{-4} bis 10^{-3} Mol/Liter, pH = 6.4 in Puffermedium) gefunden.

Die Titrierung des Komplexons durch Mn^{+2}, Co^{+2}, Ni^{+2}, Cd^{+2}, Mg^{+2}, Zn^{+2}, gibt, für dasselbe pH = 6.4 Normalamperometrische Kurven.

Im Gegenteil gewähren die Kationen der alkalinischen Erden, welche weniger stabil sind als die vorerwähnten abnorme amperometrische Kurven in dem Sinne, dass die Höhe der beobachteten Welle im Laufe der Titrierung viel grösser ist als diejenige die der Konzentration des Komplexons, welches nicht mit der Komplexverbindung verwickelt ist, entspricht.

Letztere Ergebnisse lassen sich jedoch auf genügende Weise erklären wenn man annimmt dass der gemessene Grenzstrom auf einer Seite durch die Diffusion auf der anderen Seite durch die Dissoziationsgeschwindigkeit der Komplexe in der Elektrodenumgebung festgestellt wird. Je weniger stabil die Komplexverbindung je grösser die Geschwindigkeitskonstante.

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Reçu le 21 juillet 1953

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, October 7th, 1953, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1. The President, Dr. D. W. KENT-JONES, F.R.I.C., was in the Chair, and there were 172 members and visitors present.

At this meeting there was a discussion on *Destruction of Organic Matter*.

The subject was introduced by Dr. G. ROCHE LYNCH, O.B.E., M.B., B.S., D.P.H., F.C.G.I., L.M.S.S.A., F.R.I.C., and the following two papers were presented and discussed:

The Preparation of Biological Material for the Determination of Trace Metals. Part II. A Method for the Destruction of Organic Matter in Biological Material, by G. MIDDLETON, B.Sc., F.R.I.C., and R. E. STUCKEY, B.Sc., Ph.D., F.R.I.C., Ph.C.

The satisfactory destruction of biological tissues before the determination of trace metals is often difficult, particularly when the quantities of such metals are relatively small and large amounts of organic material have to be taken. In such circumstances dry ashing presents difficulties and methods of destruction with chlorine oxy-acids are unsatisfactory. Procedures involving sulphuric acid and nitric acid often produce compounds resistant to oxidation and a method was developed in which nitric acid was the only reagent used in quantity. On heating biological material such as liver with diluted nitric acid it is dispersed in a short time with the evolution of a comparatively small quantity of oxides of nitrogen. On further heating this solution evaporates or boils until, at a certain concentration, it becomes syrupy and begins to evolve a gas, at first colourless, later brown; the mass then darkens and leaves a black "char". If this residue is treated with a small amount of nitric acid, brown fumes are evolved, the mixture swells into a froth and ultimately leaves a hard black residue. Successive repetitions of this treatment with further small quantities of nitric acid and heating on a hot-plate at 300° to 350° C result in the production of a white residue that does not char on heating. Variations of the procedure necessary for different materials were discussed. Advantages claimed for the method are that relatively small amounts of reagents are used and the temperature does not exceed 350° C. The application to the destruction of a number of organic products was described.

Determination of Lead in Foodstuffs, by H. C. LOCKWOOD, Ph.D., F.R.I.C.

The reagent diethylammonium diethyldithiocarbamate used by the sub-committee of the Society of Public Analysts and Other Analytical Chemists for the extraction of zinc (*Analyst*, 73 (1948, 304) has been found quantitatively effective with lead at a pH of 7.0. This means that lead can be extracted from solutions prepared from the ash of foodstuffs rich in phosphates at a pH at which phosphates are not precipitated. This applies particularly when magnesium is also naturally present, as with cocoa products. The lead complex is decomposed with acids and adjusted to a pH of 9. Finally, the lead is determined by extractive titration with a 0.0035 per cent. solution of dithizone in chloroform, 1 ml being approximately equivalent to 0.5 p.p.m. of lead in a 10g sample.

The procedure offers greater accuracy than is attainable with the usual sulphide technique or with the Spekker absorptiometer on dithizone solutions.

Tests on several commodities to which two or sometimes three p.p.m. of lead have been added indicate 80 to 95 per cent. recovery. Results for a number of foodstuffs were given.

BOOK REVIEWS

Qualitative analysis and analytical chemical separations, by PHILIP W. WEST, MAURICE M. VICK AND ARTHUR L. LEROSEN, The Macmillan Company, New York, 1953, 223 pages, $ 3.75.

The book is intended for students beginning courses in chemistry, chemical engineering, dentistry, medicine, geology, etc.

The authors use the classical line of approach to inorganic analysis (mainly of the cations), on the undoubtedly right grounds that although classical methods are not nowadays employed much in technical analysis, they offer pedagogical advantages, and simplify the teaching of the concepts and calculations of chemical equilibria: they claim a new approach in that the usual sulphide separations have been eliminated and replaced by a new system providing sharper and more efficient group separations. These groups are briefly (1) chloride (hot, *i.e.* Hg_2^{+2} and Ag^+), (2) basic benzoate at pH 3 to 4, (3) fluoride, (4) hydroxide, (5) amphoteric. The key to success is the early separation of tri- and tetra-valent cations.

Less than one third of the book is Experimental, the remainder being Fundamental Theory (in this order). So much emphasis is placed on equilibrium constants that a preliminary survey of these is included at the beginning of the Experimental Section.

The practical exercises, based on the new scheme of analysis, are well set out and designed to give the student not only a method of analysis but the *raison d'être* of the various devices for separating the cations.

The section of the book on Fundamental Theory is on the conventional lines, and deals with the nature of solids, liquids and solutions, stoichiometric and equilibrium reactions, equilibrium concepts applied to slightly soluble solids, weak acids and bases, hydrogen ion concentration, buffers and hydrolysis, polybasic acids and polyacid bases, coordination compounds, amphoteric substances, oxidation and reduction, and redox equilibria. The method of treatment is very suitable for the type of student to which it is addressed: it is modern in outlook, lucid, and, without being too deeply mathematical, gives a very adequate survey of the underlying principles of analytical reactions and separations. Each chapter has appropriate questions and problems (to which the answers are given).

N. STRAFFORD (Manchester)

Textbook of quantitative inorganic analysis (3rd edition) I. M. KOLTHOFF AND E. B. SANDELL, The MacMillan Company, New York, 1953, $5.00.

Most of the readers of this revue may be familiar with the earlier editions of this text. The book has been employed in many undergraduate and graduate courses in inorganic analysis in the United States.

This third revision adds little to the major portion of this excellent text with the exception of some minor additions such as the expansion of the section on physicochemical methods to include a chapter on analysis by physical methods.

The new chapter includes a general background and bibliography of many of the new physical methods of inorganic analysis. Another welcome change is the expansion of the chapter dealing with quantitative separations with a fuller treatment given to organic reagents.

This is a very well written textbook on the subject of inorganic analysis. It is designed primarily as an elementary text but the handling of the theoretical portion is satisfying even to the advanced student. Balancing the theoretical sections, there

are practical parts of the book dealing with techniques and methods. Each chapter contains a valuable bibliography and a set of practice problems.

The new edition adds little to the already excellent text. Any edition of this book is a valuable asset to a student of inorganic analysis. The new sections modernize the book somewhat and add further reason for the acquisition of this book.

A. S. POSNER (Liège)

Handbuch der Analytischen Chemie. Herausgegeben v. W. FRESENIUS (Wiesbaden) und G. JANDER (Berlin); Springer-Verlag 1953.

Von diesem Werk liegen zur Besprechung vor:

a) II, Band VII, Qualitative Nachweisverfahren der Elemente der 7. Gruppe, bearbeitet von F. FEHER, H. HECHT, W. HERR UND A. SCHNEIDER. 233 Seiten, mit 51 Abbildungen, Preis: D.M. 39.60.

b) III, Band V $a\beta$, Quantitative Bestimmungs- und Trennungsmethoden für Phosphor, bearbeitet von R. KLEMENT, 370 Seiten, mit 32 Abbildungen. Preis: D.M. 72.—.

c) III, Band VI $a\alpha$, Quantitative Bestimmungs- und Trennungsmethoden für Sauerstoff (einschl. Ozon und Wasserstoffperoxyd) bearbeitet von O. LIEBKNECHT, W. KATZ, S. KAHAN UND F. TÖDT. 342 Seiten, mit 133 Abbildungen. Preis: D.M. 66.-.

d) III, Band VIII $b\gamma$, Quantitative Bestimmungs- und Trennungsmethoden für die Platinmetalle, bearbeitet von G. BAUER UND W. GEIBEL. 118 Seiten, mit 3 Abbildungen. Preis: D.M. 24.—.

Die vier vorliegenden Bände reihen sich würdig in das hervorragende Gesamtwerk ein. Es handelt sich um ein Handbuch im wahren Sinne des Wortes. Es enthält für jedes Element sehr viele Arbeitsmethoden und Literaturhinweise. Neben den klassischen Verfahren werden die physikalischen und physikalisch-chemischen Methoden in sehr klarer und einfacher Form behandelt. Die biologische Analyse hat so an Bedeutung gewonnen, dass Spezialbearbeitungen, wie z.B. diejenige im Band V a ,,Bestimmung der Phosphorsäure im biologischen Material" von K. Lang sehr wünschenswert sind. Die Klassifizierung finden wir etwas kompliziert; es wären modernere Methoden zur Verfügung gestanden, die dem sonst so neuzeitlichen schönen Werke besser angemessen wären. — Jedem Analytiker, ob er wissenschaftlich arbeitet oder prakt. Betriebsfragen zu lösen hat, wird dieses Handbuch ein unentbehrlicher Gehilfe werden.

Y. RUSCONI (Genf)

Proceedings of the I. International Polarographic Congress in Prague, Ed. PRIROVOVEDECKE VYDAVATELSTVF.

Le premier Congrès International de Polarographie s'est tenu à Prague du 4 au 8 février 1951.

Il a remporté un grand succès et plus de 55 communications furent présentées et discutées.

En souvenir de ce Congrès et pour honorer le Professeur J. HEYROVSKÝ, le comité a publié 3 volumes importants.

Le Volume I (865 pages) comprend une série d'articles d'auteurs étrangers et un résumé d'une partie des communications inscrites au Congrès.

Le Volume II (194 pages) présente une bibliographie polarographique complète fort bien faite des années 1922 à 1950. Cette bibliographie a été revisée par J. HEYROVSKÝ.

Enfin, le Volume III (774 pages) renferme 24 articles généraux, telles que les bases fondamentales de la polarographie, le comportement polarographique des composés organiques, l'analyse polarographique organique, polarographie, biologie et médecine, etc., signés des plus grands noms de la polarographie; mise au point

fort documentée de l'état actuel de ces questions. On y trouve en outre un grand nombre de communications présentées au Congrès.

On ne saurait trop insister sur l'intérêt d'une telle publication. Elle est remarquable dans toutes ses parties et indispensable aux laboratoires qui s'intéressent à cette nouvelle et élégante méthode d'investigation et d'analyse.

D. Monnier (Genève)

Notions élémentaires de Chimie Générale à la lumière des théories modernes, par Paul Pascal. Ed. Masson & Cie. Paris, 1953, 550 pages, avec 243 figures et 7 planches, prix: FFçais. 3.600.—.

Cet ouvrage nouvellement paru, du Professeur Paul Pascal, est destiné particulièrement aux chercheurs et aux scientifiques qui désirent acquérir une idée suffisamment développée des problèmes actuels de la chimie générale. Il est particulièrement recommandé aux étudiants des facultés des sciences et de médecine. Basé sur les théories les plus modernes de la chimie générale, il donne une idée très précise de l'état actuel de cette science. Un chapitre spécial indique le moyen de lire les graphiques les plus usuels. D'autre part, grâce aux différents chapitres, qui sont indépendants les uns des autres, le lecteur pourra choisir de préférence le domaine dont il a besoin pour sa culture ou pour ses recherches. L'ordonnance de l'ouvrage permet donc à un très large public de tirer profit des dernières acquisitions de la chimie.

Nous recommandons très vivement cet ouvrage et nous nous félicitons qu'un tel volume paraisse actuellement en langue française.

Divisions de l'ouvrage:

Evolution des idées sur la nature de la matière. — La structure lacunaire et discontinue des choses. L'atome d'électricité et l'atome d'énergie. — Structure de l'atome matériel. — Les isotopes. Périodicité et altération de la distribution électronique dans l'atome. — Modification de la structure nucléaire. Transmutations spontanées. Transmutations artificielles. Isotopes indicateurs ou traceurs. — Structures moléculaires et ioniques. Classification des Structures. Géométrie des liaisons interatomiques. — Macrostructures. Substances macromoléculaires. Structures macromoléculaires. Propriété des substances macromoléculaires. Structures macroioniques. Espèces chimiques réticulaires. — Mécanisme du groupement des atomes et des ions. Liaisons de covalence. Mécanisme du groupement ionique. Mode de rupture des liaisons. Mécanisme électronique de la liaison interatomique. — La cinétique chimique. Cinétique de Van 't Hoff. Réactions homogènes. Facteurs divers de la cinétique chimique. Mécanisme de la réaction homogène. Réactions en chaîne. Propagation des réactions. Réactions photochimiques. La catalyse. — Evolution et équilibre des systèmes chimiques. L'affinité. Différents états de la matière. — Représentation graphique des systèmes. Equilibre des systèmes unaires. Equilibre des systèmes binaires. Allotropie dynamique. Equilibre des systèmes ternaires. — Etude particulière des solutions liquides. Le point de vue thermodynamique, moléculaire, ionique. — Phénomènes de surface. — Propriétés de surface des liquides. Actions directrices ou localisatrices des interfaces. Phénomènes d'adsorption. Phénomènes de membrane. Systèmes dispersés. Dispersions dans les phases gazeuses. Dispersions de liquides dans les liquides. Dispersions microcristallines dans les liquides. Dispersions macromoléculaires ou macroioniques. La notion de colloïde. Index des Auteurs. — Index des Matières.

P.-E. Wenger (Genève)

TROCKENREAGENZIEN FÜR ANALYTISCHE ZWECKE. MISCHUNGEN

von

E. DANNENBERG

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Vor einiger Zeit haben wir in dieser Zeitschrift eine Anzahl von Trockenreagenzien beschrieben, die aus Imprägnationen auf löslichem oder unlöslichem Träger bestehen und deren hervorstechendste Eigenschaften — das geringe Volumen, die vorzügliche Haltbarkeit und der geringe Preis sind. Nun gibt es aber ausserordentlich zahlreiche kompliziertere Lösungen, die sich aus Mischungen trockener Substanzen durch einfaches Übergiessen mit Wasser, Alkohol, Säure oder Alkali herstellen lassen. Sie haben die gleichen Vorteile, wie die Imprägnationen, aber im Gegensatz zu diesen lässt sich ihr Verhalten nicht von vornherein beurteilen. Bei Imprägnationen haben wir die Sicherheit, dass sie sich eben so lange halten werden, wie die feinst gepulverten Substanzen, die zur Imprägnation benutzt wurden. Bei Mischungen, die erst später in Lösung gebracht werden, kann das Resultat vorzüglich sein oder aber ein vollständiger Misserfolg. Nur der Versuch entscheidet. Kompliziert wird die Sache noch dadurch, dass oft eine Mischung anfangs ein sehr gutes Resultat ergibt und nach einigen Monaten Zersetzung eintritt. Wir haben deshalb Jahre gebraucht und viele Tausende ausgegeben. Als Endergebnis können wir einige vorzügliche Trockenreagenzien angeben und einige Grundregeln für weitere Versuche.

Im Prinzip lässt sich fast jede Lösung, die nicht gerade Zeit zur Reifung braucht, im Moment durch Auflösen der Trockenkomponenten im entsprechenden Lösungsmittel herstellen.

Besonders vorteilhaft ist diese Methode, wenn die Konzentration der Komponenten nicht kritisch ist und wenn die fertigen Lösungen schlecht haltbar oder teuer sind und noch dazu selten benutzt werden.

Sehr gut bekannt ist auch die quantitative Methode, wobei schon vorher genau abgewogene Mengen, z.B. die ,,Fixanal''-substanzen in einer grösseren Einheit Wasser z.B. einem Liter gelöst werden.

Die dritte viel weniger bekannte Art, sind die Tabletten für analytische Zwecke, die unseres Wissens nur von der englischen Firma Rydsdale für eine Serie meist metallurgischer Analysen hergestellt werden. Uns interessiert hier das, was ohne

Mitwirkung von Fabrikanten hergestellt werden kann, also die einfachen Mischungen von Pulvern.

Einteilung

Verschiedene Möglichkeiten der Einteilung sind vorhanden. Wir wollen folgende Einteilung benutzen:

1. Lösungen, die in kleinerer oder gröserer Menge durch einfaches Übergiessen der Mischung entstehen, bei denen keinerlei sekundäre Umsetzungen erfolgen.
2. Lösungen, bei denen eine sekundäre Umsetzung erfolgt.
3. Trockenreagenzien, die für die Tüpfelanalyse dienen und bei denen verschiedenartige Umsetzungen erfolgen.
4. Trockenreagenzien, die andere Umsetzungen hervorrufen, z.B. Bromide um Hypochlorit in Hypobromit zu verwandeln, Jodid-Jodatmischungen um Jod zu liefern usw.
5. Trockenreagenzien für spezielle Zwecke, wie „Densitest", um Lösungen bekannten spezifischen Gewichtes herzustellen.

Zwischen allen diesen Trockenreagenzien sind Übergänge aber keine festen Grenzen vorhanden. Eine Mischung für die Tüpfelanalyse verwandelt sich in eine gewöhnliche Lösung oft durch einfaches Auflösen in einer göseren Menge von Lösungsmittel; sekundäre Umsetzungen können durch Zusatz von Trockenreagenzien bewirkt werden in Lösungen, die man vorher durch einfaches Übergiessen erhalten hat und so fort.

Prinzip

Wenn man eine schon bekannte Lösung oder Mischung von Lösungen durch Trockenreagens ersetzen will, so frage man sich erst:

Was ist das wirkende Prinzip dieser Lösung? Ist es in alkalischem, saurem oder neutralem Medium wirksam? Welches ist der labile Anteil der Lösung? Wie stelle ich diesen labilen Anteil erst im Moment der Benutzung her?

Beispiele werden das am besten erklären.

Benedict Reagens in Pulver, besteht aus:

Kupfersulfat	17.3 g
Natriumkarbonat	100 g
Natriumzitrat	173 g

Das Reagens ist bereits im Handel und wird weitgehend zum Glukosenachweis. im Harn benutzt. Die Lösung wird durch einfaches Übergiessen hergestellt. Sekundäre Umsetzungen erfolgen bei der Auflösung, wie der Farbumschlag zeigt. Trotzdem kann man es aber eintrocknen und nacher wieder neu in Lösung bringen. Man wird das aber nicht tun, sondern einfach die Komponenten feinst pulvern, mischen und so in Flaschen füllen. Für Einzelanalysen nimmt man dann 0.3 g oder aber man bereitet beliebige Mengen von Lösung.

Folin-Wu Kupferreagens:

Kupfersulfat	4.5 g
Weinsäure	7.5 g
Natriumkarbonat	40 g

Dieses Reagens ist unseres Wissens nach nicht im Handel in Trockenform, würde aber mit grossem Erfolg so versandt werden können für all die kleinen Kliniken, etc. Hier erfolgt beim Auflösen eine Umsetzung, die nicht rückgängig gemacht werden kann, da die Weinsäure das Karbonat zersetzt. Trotzdem hält sich das Trockenreagens unbegrenzt lange und wir stellen stets einen Viertelliter Lösung durch Auflösen von 13 g zu 250 ml her. Es ist nur eine Einwage an Stelle von drei nötig, und es treten keine Verluste durch verdorbene Lösung auf.

In diesen beiden Lösungen ist das Kupferion in der alkalischen Lösung wirksam und wir können daher das Kupfersulfat durch mehr lösliche Kupfersalze ersetzen, aber auch die Weinsäure durch Glyzerin, das Karbonat durch Hyroxyd, etc. wobei die flüssigen Komponenten erst im Augenblick der Bereitung zugesetzt werden. Bei Benutzung des sehr löslichen Kupferchlorides kommt man zu 46% Lösungen, die es erlauben 10,000 Analysen pro Liter zu machen.

Betrachten wir jetzt das Nitroprussiat.

Es dient zu Reaktionen auf Sulfide, Sulfite und Aceton. Für den letzteren Zweck wird es als Trockenreagens der Rothera Zusammensetzung auf den Markt gebracht, und seine Zusammensetzung ist:

Rothera's Reagens:

Nitroprussiat	1 g
Wasserfrei Soda	50 g
Ammonsulfat	50 g

Das Reagens ist sehr gut für den Nachweis von Aceton, aber nicht unbegrenzt haltbar; wir schätzen einige Monate bis zwei Jahre. Da hier stets das Nitroprussiat in alkalischer Lösung wirksam ist kann man in verschiedener Weise versuchen ein Produkt zu erhalten, welches unbegrenzt lange haltbar ist. Da dieselben Überlegungen für andere Reagenzien gelten, geben wir sie genauer wieder.

Man kann das Nitroprussiat auf Salz imprägnieren, also 10% Nitroprussiat auf etwa 90% Natriumchlorid. Von dieser Rothera A Mischung kann man einige Körnchen zur Herstellung einer frischen Nitroprussiatlösung benutzen, die man nachher mit Ammoniak, mit Essigsäure etc. kombinieren kann, so wie es die Technik vorschreibt. Die Empfindlichkeit der Reaktion ist aber bei Gegenwart von Ammonsulfat z.B. für Aceton viel höher, sie wird ebenfalls grösser bei stärkerer Alkalität. Andererseits zersetzt sich das Nitroprussiat durch Alkali. Benutzt man:

Rothera A Reagens	Nitroprussiat	10% auf Natriumchlorid imprägniert
Rothera B Reagens	Ammonsulfat	50 g
	Natriumkarbonat	50 g

und mischt diese im Verhältnis 1 : 10, so erhält man ein ausgezeichnetes Reagens, welches Monate lang haltbar ist und das aus den unbegrenzt haltbaren Komponenten A und B in einem Augenblick hergestellt werden kann.

Das Reagens riecht aber nach Ammoniak. Wir haben daher versucht das Karbonat durch trockenes Natriumphosphat zu ersetzen. Diese Mischung riecht nicht mehr nach Ammoniak und wir vermuten daher, dass sie sehr gut haltbar sein wird.

Nehmen wir jetzt ein Benzidinprodukt für katalytische Proben. Benzidinlösungen werden hauptsächlich zum Blutnachweis benutzt, geben aber auch mit verschiedenen Metallen eine blaue Färbung. Viel besser haltbar ist das *o*-Tolidin, welches ungefähr dieselben Reaktionen gibt. Unser Trockenreagens für den Blutnachweis ist auch sehr gut zum Vanadinnachweis zu brauchen und sicherlich auch für zahlreiche andere Nachweise, die wir nicht nachprüfen konnten.

o-Tolidinreagens Dr. Dannenberg
o-Tolidin ein Teil
Weinsäure drei Teile
Bariumperoxyd drei Teile
Kalziumazetat drei Teile

Wenn man einen Tropfen Vandinlösung auf Filtrierpapier bringt, dann etwas von dem Trockenreagens daraufstreut (etwa 100 mg) und diese mit Wasser benetzt, so gibt es einen tief blauen Fleck. Dasselbe geschieht falls Blut anwesend war. Das Reagens erlaubt aber auch rohe Milch von pasteurisierter zu unterscheiden, da es mit ersterer blau wird. Dieses Reagens ist aber auch ein interessantes Beispiel dafür, dass man das Resultat bei solchen Mischungen nicht voraussehen kann. So lässt sich Tolidin nicht ohne weiteres durch Benzidin oder gar Pyramidon oder Aloin ersetzen, wohl aber kann man Strontium oder Calciumperoxyd an Stelle des Bariumsalzes nehmen. Besonders auffallend ist, dass Kupfersalze gar nicht oder sehr schlecht damit reagieren, obgleich behauptet wurde, dass die Blutreaktion eigentlich durch Spuren von Kupfer ausgelöst wird.

Warum ein Peroxyd und ein Reagens funktioniert und ein andres nicht, liegt zum Teil daran, dass bei sekundären Umsetzungen stets nur ein Gleichgewichts zustand erzielt wird, keine freie Säure, sondern eine Puffermischung, kein reines Hypobromit, sondern Mischungen mit Hypochlorit, etc.

Solche Beimischungen können von entscheidender Bedeutung für den Ablauf der Reaktion sein, ohne dass der Chemiker das voraussehen könnte.

Reagens zum Nitritnachweis:

Dieses besteht aus

α-Naphtylamin	0.1 g
Sulfanilsäure	0.5 g
Weinsäure	6 g

Das Reagens gibt bei Benetzung mit nitrithaltigem Wasser intensive Rotfärbung und ersetzt vollkommen die bekannte Lösung nach Griess. Merkwürdigerweise funktioniert es nur schlecht, wenn man Naphtylaminacetat an Stelle von Naphtylamin in der Mischung benutzt. Wenn man das Reagens nicht zur Tüpfelanalyse benutzen will, kann man eine grössere Menge zu 50 ml Wasser zusetzen, wobei dann aber mit etwas mehr Weinsäure stärker angesäuert werden muss. Unsere Mischung ist nach vier Jahren noch unverändert.

In ähnlicher Weise kann man Reagenzien durch Auflösen in Phosphorsäure statt in Wasser erhalten. Beispiel:

Folin-Wu Phospho-molybdo-wolframat Reagens:

Molybdänsäure	70 g
Natriumtungstat	10 g
Natriumhydrat	40 g

Man löst die Salze in Wasser und kocht so lange bis alles Wasser verdampft ist. Dann trocknet man bei 100 bis 120 Grad. Die obige Menge des Salzrückstandes wird mit 250 ml konzentrierter Phosphorsäure und Wasser zu einem Liter gelöst und gibt dann eine Original Folin-Wu Lösung. Wir wollen bemerken, dass bei 350 ml Phosphorsäure eine viel haltbarere Farbe erhalten wird. Das Trockenreagens eignet sich natürlich vorzüglich zum Versenden und man löst dann je 12 g zu hundert ml.

Trockenreagenzien sind Reagenzien in Konservenform und es gibt daher zahlreiche Übergangsformen, dazu gehören Trockennährböden mit oder ohne Indikatorzusatz, Puffermischungen, Standards und besondere Präparate, wie unser Densitest zur Bestimmung des spezifischen Gewichtes kleiner Flüssigkeitsmengen.

Wie zahlreich die Möglichkeiten sind zeigt der Katalog einer amerikanischen Firma (Harleco), die allein achtunddreissig sogenannte Stable Dry Pack Reagents auf den Markt bringt.

Unser „Densitest", ist etwas Neues und besteht einfach aus Natriumchlorid mit Zusatz eines geeigneten Farbstoffes, wie Erioglaucin, Erioviridin oder Fuchsin S. Es wird jedem klar sein, dass man durch Auflösen des Natriumchlorides in Mengen, wie sie in den Tabellen des Chemikerkalenders etc. angegeben sind, Lösungen des dazugehörigen spezifischen Gewichtes erhält, da die geringe Farbstoffmenge bei der Herstellung der Lösungen nicht in Betracht gezogen werden muss. So erhält man durch Auflösen von 2.00 g NaCl die 0.01 g Farbstoff in der Mischung enthalten eine Lösung die ein spezifisches Gewicht von 1.0145 bei 15°

zeigt. Sie eignet sich um Transudate von Exsudaten zu unterscheiden, indem die grüne Lösung in ersteren zu Boden sinkt und in letzteren aufschwimmt. Natürlich kann man das spezifische Gewicht beliebiger Flüssigkeiten mit einer Serie von Densitests bestimmen. Es gibt aber nur wenige Farbstoffe, die nicht ausgesalzen werden und auch nach Jahren noch nicht ausgeblichen sind und sich gegenseitig nicht ausfällen. Wir benutzen Densitest um Verwässerung von Milch nachzuweisen oder das spezifische Gewicht kleiner Harnmengen zu bestimmen.

Zusammenfassend können wir sagen, dass Trockenreagenzien die heute gebräuchlichen Lösungen entweder bei der Tüpfelanalyse ersetzen sollen, oder aber die sofortige Herstellung der gleichen Lösungen oder anderer, die für denselben Zweck dienen sollen, gestatten sollen. Genau die gleichen Lösungen zu erhalten ist nur dann möglich, wenn keine sekundären Umsätze erfolgen, was z.B. bei dem von uns angegebenen Imprägnationen der Fall ist. In allen anderen Fällen erhält man stets nur einen Ersatz, von dem nur die Erfahrung zeigen kann, ob er brauchbar oder sogar überlegen ist. Originallösungen kann man deswegen nicht erhalten, weil bei der sekundären Herstellung z.B. aus Säuren und Basen Pufferlösungen, oder aus Peroxyden und Säuren gepufferte Wasserstoffsuperoxydlösungen u.s.w. entstehen. Die Anwesenheit solcher Ionen ist aber nicht gleichgültig und nur die Erfahrung zeigt das Resultat. Wenn wir schliesslich unsere Trockenreagenzien in Tablettenform bringen, was heute schon vielfach geschieht, so erhält man eine neue quantitative Reagensform, der unserer Meinung nach eine grosse Zukunft bevorsteht. Beim heutigen Stande der Technik sind auch die einfachen Trockenreagenzien sehr interessant und oekonomisch.

Von den hier angegebenen Reagenzien haben wir das Nitro-prussiatreagens, das Tolidinreagens und das Nitritreagens in der Münchener Medizinischen Wochenschrift veröffentlicht. Das erste dient dort zum Aceton-, das zweite zum Blut- und das dritte zum Nitritnachweis im Harn. Die Erkenntnis der Zusammenhänge und der Brauchbarkeit auch für technische Zwecke ist uns aber erst jetzt gekommen.

ZUSAMMENFASSUNG

Trockenreagenzien erlauben Lösungen zu ersetzen. Wirklich identische Lösungen werden erhalten, wenn man im Augenblick der Auflösung Sekundärreaktionen vermeidet. Dies trifft zu, wenn man Imprägnationen auf unlöslichen Trägern, wie auf Körnchen benützt. In allen anderen Fällen erhält man nur einen Ersatz, der häufig befriedigende Ergebnisse zeigt. Der Grund für die Unmöglichke itidentische Lösungen zu erhalten ist, dass im Augenblick der Auflösung des Trockenreagenzes Sekundärreaktionen in der Orginallösung nicht vorhandene Ionen einführen. Diese Ionen können auf einige Reaktionen einen entscheidenden Einfluss ausüben. Es ist deshalb nicht mit Sicherheit vorauszusehen, ob die neue Lösung mit Erfolg zu verwenden ist. Trotzdem sind Erfolge zahlreich und Versuche sind zu empfehlen.

SUMMARY

Dry reagents can replace solutions. Really identical solutions are obtained if secondary reactions at the moment of dissolving are avoided. This is the case

using impregnations on insoluble carriers, like granules. In all other cases only a substitute is obtained, which frequently gives perfect results. The reason for the impossibility of obtaining identical solutions is that at the moment of dissolving of the dry reagent secondary reactions introduce ions not present in the original solution. These ions may be of decisive influence in some reactions. It is therefore impossible to foresee with security whether the new solution will be a success. Nonetheless success is frequent and trials are recommendable.

RÉSUMÉ

Les réactifs solides peuvent remplacer les solutions. On peut également procéder par imprégnation sur des supports insolubles tels que des granules, ce qui permet d'éviter des réactions secondaires au moment de la dissolution. L'emploi de réactif en solution présente l'inconvénient de faire apparaître de nouveaux ions (réactions secondaires) pouvant avoir une grande influence sur certaines réactions.

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THE TITRATION OF BISMUTH WITH COMPLEXONE III AT pH 2.0-2.8

by

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INTRODUCTION

In a previous communication[1] we described the titration of complexone with thorium nitrate at pH 2.8-4.3, using alizarin-S as an indicator. As an application of this reaction we then described the determination of Al at pH 3.5-4.3[1]: complexone is added in excess to the amount of Al and the excess of complexone is back-titrated with thorium solution using alizarin-S as an indicator.

In this communication we will describe the determination of Bi in this way.

Little is known about the complex-forming properties of Bi with complexone. PRIBIL AND MATYSKA determine Bi at pH 2 with complexone by means of amperometric titration[2].

SCHWARZENBACH describes a method of titrating Bi at pH 7 with complexone using $[BiJ_4]^-$ as an indicator; at the end-point the yellow colour of the $[BiJ_4]^-$ complex is destroyed in favour of the Bi-complexone[3].

It appeared that Bi forms a very strong complex with complexone even at pH 2. On the other hand it was also possible to titrate complexone-thorium at pH 2; thorium still forms stable complexes with complexone at pH 2.

Schematically the reaction between bismuth and complexone is represented by $Bi^{+3} + Y^{-4} \rightleftharpoons BiY^-$, where Y^{-4} denotes the anionic part of complexone (H_4Y).

EXPERIMENTAL PART

Reagents

All reagents c.p. quality. Deionised water should preferably be used.

Complexone III 0.05*M:*

18.6 g of disodium salt of ethylenediaminetetra-acetic acid is dissolved and diluted to 1000 ml.

Thorium nitrate 0.05*M:*

27.6 g of $Th(NO_3)_4.4H_2O$ is dissolved and diluted to 1000 ml.
Both solutions are standardised according to the method described in[1].

Alizarin-S indicator, 0.1%*:*

0.1 g alizarin-S is dissolved and diluted to 100 ml.

Bi-standard solution, 10 mg Bi/ml*:*

10 g pure Bi metal was dissolved in HNO_3 and, after boiling out and cooling, diluted with HCl 1 : 2 to 1000 ml.

Titration curve of Bi-complexone with NaOH

A solution containing 0.8 m*M* Bi and 0.8 m*M* complexone was titrated with NaOH, the pH being measured by means of a glass-calomel electrode and a Philips pH-meter. In a second experiment a solution with 0.8 mMol Bi and 1.6 mMol complexone was titrated. (The volume was about 100 ml; no KCl was added and no special precautions were taken to exclude CO_2 from the solutions.)

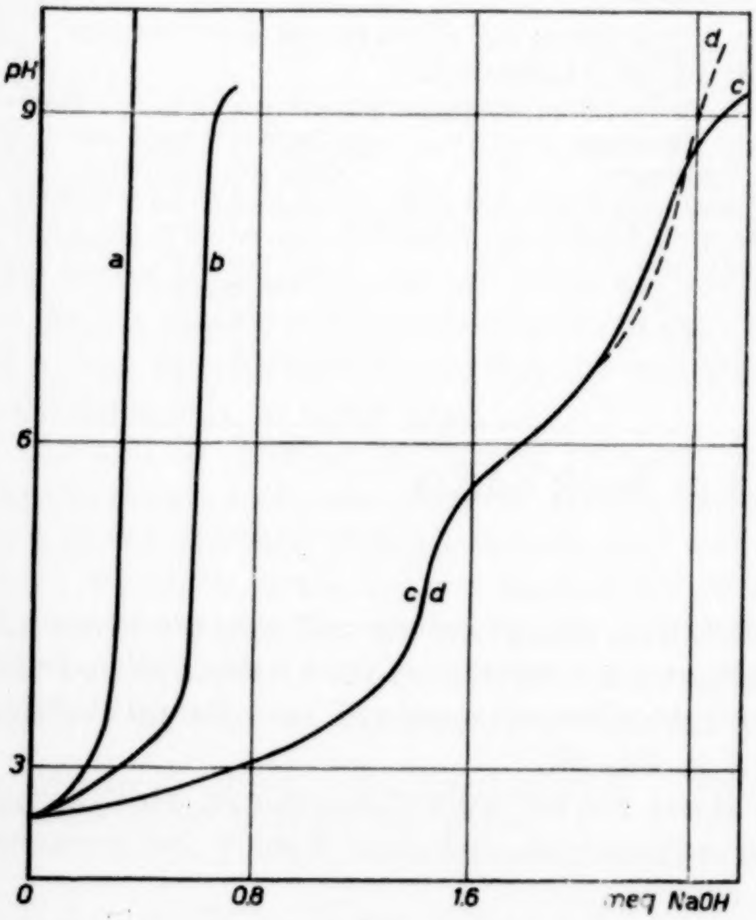

Fig. 1. Titration curves with NaOH of
(a) HCl
(b) Bi-complexone 0.8 mmol each
(c) Bi-complexone 0.8 mmol Bi, 1.6 mmol complexone
(d) complexone

From the graphs in Fig. 1 it can be concluded that Bi forms a very strong complex with complexone, as there is only a small difference between the curves of pure HCl and of Bi-complexone (ratio 1 : 1).

Moreover Bi forms no higher complexes with complexone (*cf.* curve b and c). Above pH 8 hydrolysis of the Bi-complexone takes place.

Judging from the graphs, it would not be possible to titrate Bi at a pH below, say, 5; from experiments, however,

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it appeared possible to titrate Bi even at pH 2, both by the method of excess complexone-back titration with thorium nitrate and by a direct titration (in the presence of much tartrate and using thiourea as an indicator).

Titration of complexone with thorium nitrate at pH 2.0

It appears possible to titrate complexone with thorium nitrate at pH 2.0 by omitting the buffer solution. One gets a very distinct end-point. The reason why we did not succeed in titrating complexone-thorium nitrate at pH 2.0 with the experiments, described in the earlier publication[1], lies in the fact that monochloroacetic acid-sodium acetate hinders the reaction at this pH. In Table I may be found some results of the titrations of complexone with thorium nitrate; the complexone solution in a volume of about 100 ml was brought to pH 2.0 by means of 2N HCl or 2N NH_4OH and titrated with thorium nitrate, 1½ ml of alizarin-S solution as an indicator.

TABLE I

TITRATION OF COMPLEXONE III WITH THORIUM NITRATE pH 2.0, VOLUME ABOUT 100 ml, 1½ ml ALIZARIN-S.

ml complexone 0.0490 M	ml thorium nitrate	molarity found for thorium solution
10.00	9.53	0.0514
20.00	19.08	0.0514
30.00	28.46	0.0517
		$\bar{x}$ = 0.05150

Molarity Th solution at pH 2.8-4.3 found: 0.05145

Titration of bismuth

We performed two series of titrations, one at pH 2.0 and another at pH 2.8. After the addition of excess complexone the solution at pH 2.8 was buffered with 5 ml monochloroacetic acid 2M-5 ml sodium acetate 1M per 100 ml volume, that of pH 2.0 was only adjusted to this pH.

The solutions, in a volume of about 100 ml, were then titrated with thorium nitrate and 1½ ml alizarin-S as an indicator; the end-point is sharp and is reached when the solution becomes red-orange.

In this series we also performed some titrations with increasing amounts of excess complexone; the results were the same whether a great excess was present or not.

From the reaction between Bi and complexone, it follows that 1 ml 1M complexone is equivalent to 104.5 mg Bi.

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TABLE II

TITRATION OF BISMUTH WITH COMPLEXONE-THORIUM NITRATE AT pH 2.0 AND 2.8

pH 2.0			pH 2.8		
mg Bi present	mg Bi found	△ in mg	mg Bi present	mg Bi found	△ in mg
55.7	55.7	0	27.85	27.9	+0.05
111.4	111.8	+0.4	55.7	55.8	+0.1
167.1	167.0	—0.1	111.4	111.4	0
278.5	278.2	—0.3	167.1	166.0	—1.1
			278.5	279.3	+0.8

When titrating Bi at pH 2.8, the end-point remains stable; but at pH 2.0 the colour fades after standing for 10 minutes; this effect is very pronounced when heating the solution, since part of the Bi is even hydrolysed and precipitated.

INTERFERENCES

Of the cations we investigated the influence of Ni and Fe, Al, Pb, Cd, Zn and Cu, Mn and Co, Mg, Ba and Ca, both at pH 2.8 and 2.0. At pH 2.8 and 2.0 there is no interference of Co and Mn (10 mg), Mg, Ca and Ba (40 mg).

At pH 2.8 Fe and Ni react quantitatively, Al does nearly so. Cu, Pb, Zn and Cd interfere seriously, though unfortunately not quantitatively.

At pH 2.0 Fe still reacts quantitatively, but there is no interference of Al (30 mg), Pb, Zn and Cd (100 mg). Ni still interferes seriously, and Cu (100 mg) interferes only to about 5%.

Sn and Sb interfere by forming precipitates. It may be possible to titrate Bi in the presence of these elements using a direct titration with complexone at pH 2.0 in the presence of much tartaric acid and thiourea as an indicator; tartaric acid interferes in the indirect method by giving an indistinct end-point. A few titrations on pure Bi solutions performed in this way showed promise, but the method is still to be investigated more exactly.

For the influence of anions we refer to literature[2].

We are indebted to the directors of N.V. Philips Gloeilampenfabrieken for their permission to publish this paper.

SUMMARY

A titration procedure for Bi is described; by adding an excess of complexone III (Versene) and back-titrating at pH 2.0-2.8 with standard thorium nitrate solution using alizarin-S as an indicator, it is possible to determine Bi with a precision of about 0.3%.

By choice of the proper pH it is possible to eliminate most of the interfering elements, but at pH 2.0 Fe and Ni still interfere, and Cu only to a slight extent.

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Attention is drawn to the fact that it may be possible to determine Bi at pH 2.0 by direct titration with complexone III in the presence of much tartrate, using thiourea as an indicator. This method might be of value in the presence of Sn and Sb.

RÉSUMÉ

Une méthode de titration du bismuth est décrite. Par addition d'un excès de complexon III et titration en retour au pH 2.0-2.8, par une solution étalon de nitrate de thorium, en présence d'alizarine S comme indicateur, il est possible de doser le bismuth avec une précision d'environ 0.3%. En choisissant un pH convenable, on peut éliminer les interférences d'un grand nombre d'éléments, cependant au pH 2.0, Fe et Ni gênent encore, et Cu seulement légèrement. L'auteur attire l'attention sur le fait qu'il peut être possible de doser Bi au pH 2.0, par titration directe au moyen de complexon III, en présence de grandes quantités de tartrate, en utilisant la thiourée comme indicateur. Cette méthode est avantageuse lorsqu'on est en présence de Sn et Sb.

ZUSAMMENFASSUNG

Es wird ein Titrationsverfahren zur Bestimmung von Wismut beschrieben. Durch Zugabe eines Überschusses von Complexon III (Versene) und Rücktitration bei pH 2.0-2.8 mit einer geeichten Thoriumnitratlösung und Alizarin S als Indikator ist es möglich Wismut mit einer Genauigkeit von ungefähr 0.3% zu bestimmen.

Durch die Wahl eines geeigneten pH's ist es möglich die meisten der störenden Ionen auszuschalten, bei pH 2.0 stören aber Eisen und Nickel und in einem geringen Ausmass Kupfer immer noch.

Es wird darauf aufmerksam gemacht, dass es möglich wäre Wismut bei pH 2.0 durch direkte Titration mit Complexon III in Gegenwart von viel Tartrat mit Thioharnstoff als Indikator zu bestimmen. Diese Methode könnte bei Gegenwart von Zinn und Antimon von Wert sein.

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ON THE VOLUMETRIC DETERMINATION OF HYDROGEN SULFIDE AND SOLUBLE SULFIDES

by

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Methods using iodine as the oxidizing agent

The iodometric determination of sulfide is based on the reaction:

$$H_2S + I_2 = S + 2H^+ + 2\ I^-$$

which takes place in an acid media. In an earlier communication[1] methods based on this reaction were discussed, some common sources of error were found, and principles for avoiding these errors were given. One of the critical points was the mixing of the sulfide solution, which naturally must be alkaline, with the acid iodine-containing medium. Most methods found in the literature[2-6] recommend that the sulfide solution should be added to an acidified iodine solution, and not the reverse. In this way the side-reaction

$$S^{-2} + 4I_2 + 8\ OH^- = SO_4^{-2} + 8I^- + 4H_2O$$

does not take place to any considerable extent. In one method of ZIMMERMANN[7], however, a cadmium acetate-sodium acetate absorbent containing the sulfide is added to a neutral potassium iodide-iodate mixture, which is then acidified. It may seem probable that the slightly soluble cadmium sulfide precipitate would not react in this solution, which has a pH value of about 8, but will only react when the pH is lowered by an addition of acid. As this method is recommended as the final step in a general analysis method[7] for sulfur in organic substances and rather strongly differs from the other methods, it appeared interesting to make an investigation concerning its accuracy.

In order to avoid losses of hydrogen sulfide, all experiments were carried out in the vacuum flask described before[1]. All reagents were added through the funnel and sucked into the flask, which was not opened before the last reagent was added. After each addition the funnel was rinsed with distilled water and the flask was shaken. The following reagents were used:

Sodium sulfide solution
Potassium iodide solution, 10%

Potassium iodate solution, 0.02*N*

Hydrochloric acid, 1 : 1

Cadmium-acetate solution (50 g cryst. cadmium acetate and 400 g sodium acetate were dissolved in one liter distilled water).

The sodium sulfide solution was prepared according to KIRSTEN AND CARSTENS[9] and standardized in two ways, by the titration method described before[1], and by total oxidation with hydrogen peroxide and precipitation with barium chloride. These two standardisations coincided within 0.1%. All titrations were carried out with a carefully standardized, 0.01*N* sodium thiosulfate solution.

The first experiments were carried out mainly according to the method of Zimmermann: Two ml of potassium iodide solution and 15 ml of potassium iodate solution were sucked down into the flask. Then 10 ml of cadmium acetate solution and 15 ml of the sulfide solution were mixed in the funnel and sucked down. Finally 20 ml hydrochloric acid were added quickly in the same way. The following results were obtained:

Milligrams of sulfur found:	3.025	3.055	3.049
Milligrams of sulfur added:	2.975	2.975	2.975
Yield, per cent.:	101.7	102.7	102.5

The values are somewhat high. In order to find any critical point the method was altered slightly in several ways and it was found, as indicated by ZIMMERMANN[8], that the speed with which the hydrochloric acid was added was of importance. In some experiments the acid was added slowly, drop by drop, and then the following figures were obtained:

Milligrams of sulfur found:	3.298	3.249	3.333
Milligrams of sulfur added:	2.975	2.975	2.975
Yield, per cent.:	110.9	109.2	112.0

The results are poorly reproducible and about ten per cent. too high. Apparently the pH value of the solution changed slowly and unevenly, and partial oxidation to the sulfate state was the result. If the method of ZIMMERMANN is followed strictly, the funnel should be rinsed with a mixture of one ml potassium iodate solution, a few drops of potassium iodide solution and 20 drops of hydrochloric acid, before the rest of the acid is added. This produces errors of the same type:

Milligrams of sulfur found:	3.060	3.157	3.154	3.092
Milligrams of sulfur added:	2.975	2.975	2.975	2.975
Yield, per cent.:	102.9	106.1	106.0	103.9

In other experiments it was found that even the amount of potassium iodide added was critical. When only 0.5 ml of potassium iodide solution were used instead of 2 ml, the following results were obtained:

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Milligrams of sulfur found:	3.440	3.440	3.419
Milligrams of sulfur added:	2.975	2.975	2.975
Yield, per cent.:	115.6	115.6	114.9

Even in this case the values obtained are again much too high.

In further experiments the method was changed to be in accordance with the principles given before[1], without changing the compositions or the amounts of the reagents. Thus the reagents were added in the order: hydrochloric acid, potassium iodide and potassium iodate in mixture, and sulfide-containing cadmium-acetate solution. The results obtained were:

Milligrams of sulfur found:	2.972	2.978	2.975
Milligrams of sulfur added:	2.975	2.975	2.975
Yield, per cent.:	99.9	100.1	100.0

As can be seen the results were accurate within experimental limits.

It may be concluded that mixing of iodate and sulfide solutions in a weakly alkaline media causes side reactions, which sometimes produce errors in the iodometric determination of sulfides, and that these errors are avoided, if the mixing takes place in an acid media. The results are in agreement with those of earlier experiments of Kirsten and Carstens[9].

ACKNOWLEDGEMENT

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SUMMARY

Two procedures for the determination of sulfides are compared. In one, the sulfide, contained in a weakly alkaline cadmium acetate solution, is added to a neutral solution containing potassium iodide and potassium iodate, which is then acidified. It is shown that, when this order is followed, errors are introduced, which are probably due to the partial oxidation of sulfide to sulfate instead of to elemental sulfur. In the other method the sulfide in the cadmium acetate solution is added first to an acid solution, followed by the addition of the potassium iodide-iodate solution. The theoretical yield was obtained.

RÉSUMÉ

Comparaison de deux méthodes de dosage des sulfures.

1ère méthode: Une solution légèrement alcaline renfermant le sulfure et de l'acétate de cadmium est ajoutée à une solution neutre d'iodure et d'iodate de potassium. Puis on acidifie. Il est démontré qu'en suivant cet ordre, des erreurs sont introduites, elles sont dues probablement au fait que le sulfure est oxydé en sulfate au lieu d'être oxydé en soufre élémentaire.

2ème méthode: le sulfure dans la solution d'acétate de cadmium est additionné d'une solution d'acide, puis d'une solution iodate-iodure. Les résultats ainsi obtenus sont théoriques.

ZUSAMMENFASSUNG

Zwei Methoden für die Bestimmung von Sulfiden werden verglichen. Bei der ersten Methode wird das Sulfid, das sich in einer schwach alkalischen Cadmiumacetatlösung befindet, zu einer neutralen Lösung von Kaliumjodat und Kaliumjodid gegeben. Die Lösung wird dann angesäuert und der Überschuss an Jod bestimmt. Es wird gezeigt, dass bei Zusatz der Reagenzien in dieser Reihenfolge Fehler entstehen, die wahrscheinlich darauf beruhen, dass ein Teil des Sulfides zu Sulfat statt zu elementarem Schwefel oxydiert wird. Bei der anderen Methode wird die sulfidhaltige Lösung zuerst angesäuert und dann mit Kaliumjodid-jodatlösung versetzt, wobei theoretische Ausbeuten erhalten werden.

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THE DETERMINATION BY RADIOACTIVATION OF THE OXYGEN CONTENT OF POWDERED METALS WITH PARTICULAR REFERENCE TO BERYLLIUM

by

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INTRODUCTION

To the conventional techniques of oxygen determination in certain metals such as the vacuum fusion[1], chloride volatilisation[2], amalgamation[3], hydrogenation[4], selective dissolution[4], difference from determined metal content[5] and reaction with sulphur vapour[6] methods, has recently been added the nuclear technique of KIRSHENBAUM AND GROSSE[7] the basis of which is isotopic dilution of a sample of gas enriched in ^{18}O by the oxygen present in the metal sample, the dilution being measured mass spectrometrically. Not all the above mentioned techniques are readily applicable to beryllium metal and another nuclear approach was investigated, that of radioactivation. A suggestion was made in a review by one of the present authors[8] about four years ago that the nuclear reaction ${}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}He + {}^{3}_{1}H, {}^{16}_{8}O + {}^{3}_{1}H \rightarrow {}^{18}_{9}F + {}^{1}_{0}n$ might be made the basis of a method of detection of either lithium ($t_{\frac{1}{2}}$ 112 m) or oxygen, neither of which elements form very suitable radionuclides by the normal n, γ type of reaction. The work described in this paper was carried out in an attempt to put this suggestion on to a practical basis, using the Harwell Pile as the neutron source.

DIRECT NEUTRON REACTIONS ON OXYGEN ISOTOPES

Before going on to deal with the lithium reaction, the possibilities of direct neutron reactions can be briefly discussed. The value for the isotopic activation cross section for the reaction $^{18}O(n,\gamma)^{19}O(t_{\frac{1}{2}}$ 27 sec) is given as $2.2 \cdot 10^{-4}$ barns, and was approximately confirmed by irradiation of sucrose in the Harwell Pile followed by resolution of the resulting (complicated) decay curve. Thus at a counting geometry of 12%, an irradiation for one and a half minutes gave a ^{19}O activity of 120 c/m/mg oxygen. The actual value of the extrapolated half life was usually between 20 and 23 seconds.

It was noticed that there persisted in all the decay curves obtained, an activity with a half life of between 100 and 140 seconds. This might be due to an(n, 2n) reaction on ^{16}O giving ^{15}O, which is a positron emitter with a half life of 118 seconds, but was not confirmed. More detailed investigation of both the above reactions was not carried out as irradiation of a typical sample of beryllium metal demonstrated that activity arising from impurities present effectively "swamped" that from any oxygen radionuclides, and of course chemical separations were not feasible in view of the short half lives involved. Resolution of the first part of the decay curve for one sample of irradiated beryllium metal in fact showed that three separate activities contributed to the total, the first two of these having 2.3 and 36 minute half lives, probably corresponding approximately to 0.03% aluminium and 0.07% chlorine impurities respectively.

SECONDARY NEUTRON REACTION WITH OXYGEN

The production of neutron deficient radionuclides by pile irradiation using the $^{6}_{3}Li$ (n, α)t reaction as the source of tritons for (t, n)reactions is now well known. Thus pile irradiation of lithium carbonate has been used for the production of ^{18}F by following reaction: $^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{3}_{1}H$; $^{16}_{8}O + ^{3}_{1}H \rightarrow ^{18}_{9}F + ^{1}_{0}n$. The problem of applying this (t, n) reaction to the determination of oxygen in metals is to obtain reproducibly some quantitative relationship between the oxygen present and the ^{18}F yield, when not only are the lithium and oxygen in different compounds, but the oxygen is present in small amounts in metal particles of finite size. A triton has thus to travel through a certain thickness of both lithium compound and metal sample before it meets an oxygen atom with which it can react and give ^{18}F.

In the lithium reaction the triton recoils with an energy of about 2.7 MeV, which is sufficiently near to the potential barrier of ^{16}O (3.2 MeV for singly charged particle, calculated from E_B (MeV) $= \frac{Z}{A^{1/3}}$ [9]), to give some yield of ^{18}F. The range in air of a 2.7 MeV triton is given by POLLARD AND DAVIDSON[10] as approx. 6 cm and if the formula of EVANS[11] for the range of α particles in a medium is applied to the case of tritons (which it can be approximately) then the range in beryllium will be given by

$$R_{Be} = 3.2 \times 10^{-4} \frac{(R\ \mathrm{air})}{P} A^{1/3}\ \mathrm{cm}$$

where $R_{air} = 6$ cm; P = density of beryllium = 1.85 g/cm^2
A = atomic weight of beryllium = 9
i.e. $R_{Be} \approx 0.003$ cm

Now if only the beryllium sample is considered as absorbing the available tritons, *i.e.* that each particle of metal is surrounded by the lithium salt giving rise to the flux of tritons, and remembering that practically all the latter have similar range, then at least they will reach oxygen atoms in the sample provided the particle radius is not greater than 30 microns *i.e.* particle size $<$ 60 microns. The tritons are of course losing energy during their passage through the beryllium particle and therefore the probability of their reaction with oxygen atoms decreases with distance into the particle. The effect of this on the determination is minimised by simultaneous irradiation of standards of similar particle size to the sample.

Samples on which the work described below was carried out consisted of material of particle size almost entirely less than 50 microns.

EXPERIMENTAL

Radiochemical separation

As mentioned earlier, the beryllium samples to be analysed contain impurities giving rise to radioactivity on pile irradiation and therefore radiochemical separation of the ^{18}F was necessary. The method adopted involved distillation of the fluoride as hydrofluosilicic acid in the presence of carrier, followed by precipitation of lead chlorofluoride, which was finally dried and counted. Because of the presence of chloride impurity, which gave rise to ^{38}Cl with a half life of 38 minutes and which followed fluorine in this separation, an intermediate scavenging precipitation of silver chloride was inserted after the distillation. The complete chemical operation up to the point of counting the final lead chlorofluoride precipitate occupies 3-4 hours and the product has always given a satisfactory decay curve of 112 ± 2 minutes, showing adequate radiochemical purity.

Self-absorption correction

^{18}F is a positron emitter of maximum energy only 0.64 MeV, and therefore self-absorption in the sample is an important consideration. A correction graph for this purpose was obtained by preparing sources of lead chlorofluoride of

TABLE I

^{18}F SELF-ABSORPTION CORRECTION IN LEAD CHLOROFLUORIDE PRECIPITATES

	"A"			"B"			"C"	
Weight PbClF g	Activity (c/m)	Correction factor	Wt. PbClF	Act.	Corr. factor	Wt. PbClF	Act.	Corr. factor
0.372	1820	0.48	0.264	2180	0.40	0.658	616	0.74(5)
0.610	1395	0.63	0.510	1461	0.59	0.876	503	0.91
0.865	925	0.95	0.758	1133	0.76	0.985	456	1.01
1.109	852	1.03	1.003	856	1.01	1.108	431	1.06
1.349	652	1.35	1.252	739	1.17	1.268	367	1.25
1.566	617	1.43	1.989	457	1.89	1.486	346	1.33
1.768	520	1.69						
2.078	470	1.87						

different weights but containing the same activity of ^{18}F. The results are shown in Table I and in Fig. 1. All activities measured subsequently were corrected for variation in source weight to a standard weight of one gram of lead chlorofluoride on the counting tray by using Fig. 1.

Choice of lithium salt

The essential requirements in the lithium salt to be used as a source of tritons are (a) absence (or minimum) of oxygen (b) non-hygroscopicity (c) small particle size. Lithium fluoride seemed most suitable and had the added advantages that fluorine itself gives only a 12 sec half life activity on neutron irradiation, with a very low cross-section; and also of providing the carrier required for the chemical separation. There remained the possibility of a (n, 2n)reaction on the fluoride to give ^{18}F but this was proved to be of no importance by the negligible yield of ^{18}F obtained from irradiated sodium and ammonium fluorides.

Even without adding an oxygen containing substance, irradiated samples of lithium fluoride gave a certain amount of ^{18}F and since this can only be due to the presence of oxygen in the lithium fluoride itself, various samples and treatments were tried to overcome or diminish this effect. "Extra-pure" B.D.H. lithium fluoride was found to be the most satisfactory, and further treatment of this by gentle heating in a covered platinum crucible until the powder was partially sintered but not quite melted, improved the material further. The sintered mass was cooled in a vacuum desiccator, powdered in an agate mortar, and finally stored in the desiccator. Even so it has not so far been possible to obtain lithium fluoride with an "oxygen-equivalent" content of less than about 0.2% and this is the limiting factor at present from the viewpoint

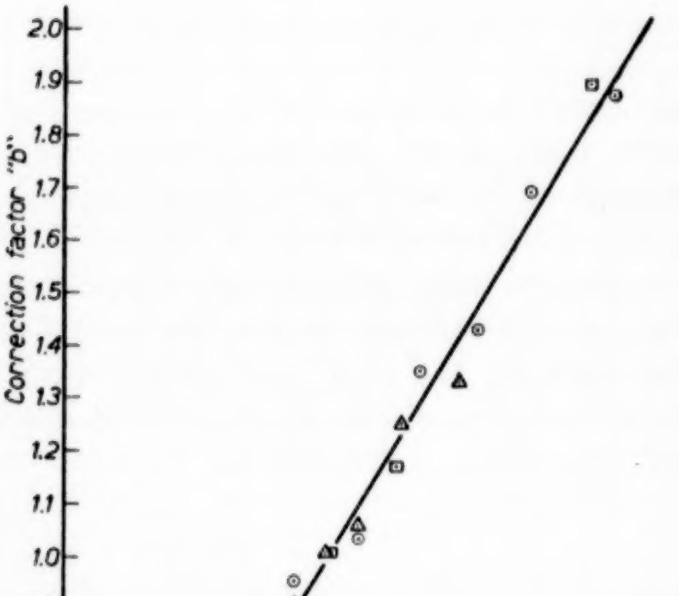

Fig. 1. Correction graph for β self-absorption in lead chlorofluoride sources. A certain activity appearing as A c/m in a source of m grams PbClF will appear as (A × b) c/m in 1 gram PbClF where b refers to m grams.

of sensitivity of the activation method. It should be noted that the use of secondary neutron reactions, as in this case, introduces the problem of 'blanks', normally absent from radioactivation analysis.

It has been convenient to refer all measured activities to a certain set of conditions ("normal conditions") these being 100% chemical yield from 126 mg lithium fluoride, corrected for self-absorption losses, at 240 minutes after the end of a 30 minute irradiation, with a counter geometry of 10.6%. Values of the activity under these "normal" conditions for different samples and treatment of lithium fluoride are shown in Table II.

TABLE II

'STANDARD ACTIVITY' OBTAINED FROM DIFFERENT LiF MATERIALS

Sample	Activity ("normal" conditions) c/m	Average value
Normal LiF	3500, 3980, 4480, 4790	4190
,, (fused in Pt crucible)	2700, 4210, 6860	4590
,, (sintered)	1000, 1140	1070
"Extra-pure" LiF	2610	
,, (fused)	1580	
,, (sintered 1st sample)	640, 720, 820, 910	770
,, (,, later samples)	175-247 (20 results)	205

Normally, irradiation of the lithium fluoride was carried out in sealed polythene tubing, but replacement of polythene by aluminium foil, or of the air in the irradiation tube by nitrogen, caused no significant diminution of the activity from a batch of lithium fluoride. It seems clear that there is in fact some combined oxygen in the materials examined so far. Other lithium halides tried showed no improvement.

Neutron self-shielding

In cases where the neutron absorption cross-section σ of an irradiated element is high there is the possibility of a self-shielding effect, the effective neutron flux at the centre of the material being considerably reduced. Since lithium has a fairly high value for σ (67 barns) it was necessary to check that such an effect was insignificant in these experiments. This was confirmed by irradiating portions of the fluoride mixed with increasing quantities of powdered graphite, the latter having relatively low absorption cross-section. The fact that no increase in activity of ^{18}F was found on dilution with graphite demonstrates that self-absorption was insignificant.

TABLE III

EXPERIMENTS TO MEASURE SELF-SHIELDING EFFECT IN IRRADIATED LiF

Experiment	$\frac{\text{Graphite}}{\text{LiF}}$ ratio		activity (c/m) under set conditions
A	1:1	No Graphite	224
		With ,,	218
B	2:1	No Graphite	175
		With ,,	175

LiF-Be ratio

It is obvious that the yield of ^{18}F from a given mass of oxygen irradiated with lithium in a certain flux of neutrons will depend to some extent on the lithium: oxygen ratio. To find a suitable ratio, quantities of beryllium metal powder known to contain about 1% oxygen were intimately mixed with different amounts of lithium fluoride and irradiated. The results are shown in Table IV and plotted in Fig. 2. A ratio of 7:1 was used for subsequent work, and some idea of the reproducibility attainable was gained by carrying out five experiments with 18 mg samples of beryllium mixed with 126 mg LiF. Activities obtained were as follows: (counting efficiency 10.6%, source weight 1 g, 240 minutes after 30 minutes irradiation) 581, 593, 595, 591, 604 c/m, average 593.

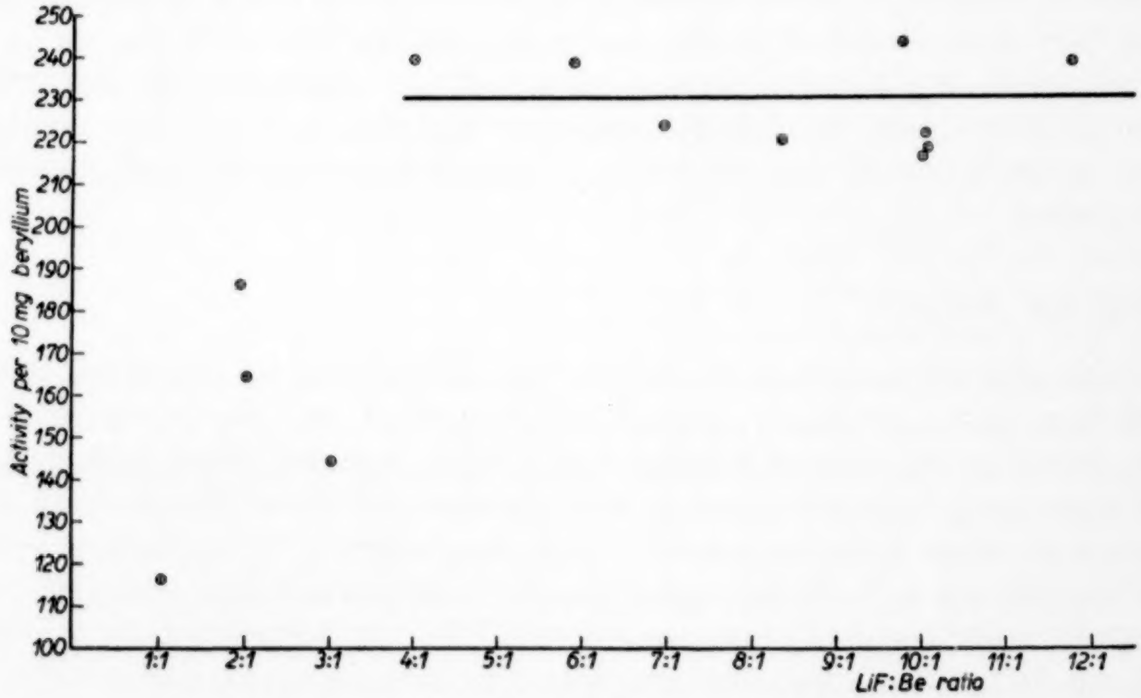

Fig. 2. Lithium fluoride-beryllium ratio experiments.

TABLE IV

EXPERIMENTS TO FIND SUITABLE LiF:Be RATIO

LiF:Be ratio	LiF(mg)	Be(mg)	LiF activity (A_1) (arbitrary units)	Total activity (A_2)	A_2-A_1	Activity per 10 mg Be
1.04	125.1	120.3	209	1601	1392	116
1.94	125.5	62.7	261	1425	1164	186
2.04	117.4	57.5	182	1127	945	164
3.01	125.5	41.7	192	791	599	144
4.01	121.5	30.3	189	914	725	239
5.94	122.0	20.5	205	696	491	238
6.97	126.8	18.2	213	618	405	223
8.35	118.6	14.2	181	493	312	220
9.78	122.4	12.5	206	510	304	243
10.03	248.9	24.8	358	893	535	216
10.03	248.8	24.8	396	942	546	221
10.06	240.5	23.9	373	893	520	218
11.76	123.4	10.4(5)	189	437	248	238

RESULTS

As in other applications of radioactivation, simultaneous irradiation of samples with a standard is practised for this oxygen determination, in addition, in this case, to the "blank" lithium fluoride. Initially, beryllium oxide mixed with a beryllium metal sample, was used as the standard but once the oxygen content of a suitable metal was established by this means, this metal itself was preferred.

Detailed results of a series of experiments are given in Table V.

TABLE V

DETAILED RESULTS OF LiF AND BERYLLIUM IRRADIATIONS

Mixture irradiated	^{18}F Activity ("normal" conditions)
126 mg LiF (4 expts.)	214, 188, 201, 202 (av. 201)
126 mg Lif + 18 mg Be (sample A)	446, 434, 460, 424 (av. 441)
,, + ,, + 0.678 mg oxygen (present as BeO)	1166
,, + ,, + 1.207 "	1776
,, + 18 mg Be (sample B)	276

From Table V the activity per mg of oxygen can be calculated as follows:
0.678 mg oxygen gives an activity of (1166—441) = 725 c/m or 1,069 c/m/mg
1.207 mg ,, ,, ,, ,, ,, (1776—441) = 1335 c/m or 1,107 c/m/mg
giving as an average that 1 mg of oxygen is equivalent to 1,088 c/m.

From this the oxygen content of the beryllium metal sample A can be calculated:
18 mg of sample gave an activity of (441—201) = 240 c/m

$$\therefore \text{ oxygen content } = \frac{240}{1088} \times \frac{100}{18} = 1.2(3)\%$$

$$\text{Similarly sample B contains } \frac{(276\text{-}201)}{1088} \times \frac{100}{18} = 0.3(8)\%$$

or alternatively using sample A as the standard.

$$\frac{(276\text{-}201)}{240} \times 1.23 = 0.3(8)\%$$

The oxygen content of the lithium fluoride itself can be estimated approximately similarly:

$$\frac{201}{1088} \times \frac{100}{126} = 0.15\%$$

although it should be pointed out that the tritons are probably more efficiently used in converting, to ^{18}F, oxygen occurring in the lithium fluoride, than that occurring in the beryllium oxide standard, as mentioned earlier.

Further determinations on sample A confirmed the figure obtained previously so that it is possible to give a final figure for this sample of 1.2 ± 0.1% oxygen (6 determinations). The final figure for sample B is 0.34 ± 0.05% oxygen (7 determinations).

Although work on other methods of determination of oxygen in beryllium is still proceding comparison with their results on these two samples is illustrated in Table VI.

TABLE VI

COMPARISON OF RESULTS ON SAMPLES A & B OBTAINED BY DIFFERENT METHODS

Method	% oxygen	
	A	B
Vacuum fusion[A]	0.9 ± 0.3	0.31 ± 0.08
Hydrogen evolution[B] (BeO by difference)	1.3	—
Chlorine volatilisation[B]	1.5 — 1.6	0.47
Hydrogen chloride volatilisation[B]	1.1	0.39
Copper sulphate solution[B]	1.3	0.45
Radioactivation	1.2 ± 0.1	0.34 ± 0.05

A. by J. N. Gregory and D. Mapper, Analytical Chemistry Group, A.E.R.E.
B. by F. J. Bryant, Chemical Inspectorate, Woolwich.

DISCUSSION

From the figures for activity per mg of oxygen given in the preceding section, it is possible to calculate a very approximate "effective cross-section" for the lithium-oxygen reaction and the value obtained, assuming a flux of 10^{12} neutrons/cm^2/sec during the irradiation of the standards, is half a millibarn. As mentioned earlier, however, low though this cross section is, it is not at present limiting sensitivity. The oxygen content of the lithium fluoride is much more limiting particularly when it is recalled that seven times as much lithium fluoride as beryllium metal sample, is taken. With the best lithium fluoride used in this work the effective lower limit for oxygen in beryllium would seem to be 0.1-0.2%, depending on the homogeneity of, and the precision of the 'blank' values obtained for, the lithium fluoride.

The other limitation of this activation method is that it is only applicable to finely divided powder. Nevertheless the method has served a useful purpose in a collaborative project for investigating several possible methods for the determination of oxygen in beryllium.

APPENDIX

The determination of oxygen in beryllium metal powder by radioactivation

Outline of method

The powdered metal sample is mixed with lithium fluoride and irradiated in the Harwell Pile. The mixture is then dissolved in sulphuric acid and the fluorine distilled as hydrofluosilicic acid. After a scavenging precipitation to remove active chlorine, lead chlorofluoride is precipitated and the fluorine activity determined on a normal β counter.

Special reagents

Powdered lithium fluoride prepared by sintering "extra pure" B.D.H. reagent in a platinum crucible followed by grinding in an agate mortar. The reagent is stored in a vacuum desiccator.

Apparatus

Four sets of distillation apparatus for normal fluorine distillation purposes.

Procedure

1. Weigh out about 18 mg (± 0.3 mg) of beryllium sample and 7 times this weight of lithium fluoride. Add the fluoride to the beryllium in a weighing bottle and mix well. Transfer as much as possible of the mixture to a polythene tube (int. diam. 5 mm ext. diam. 7 mm) and seal as near to the packed mixture as possible. Treat the standard beryllium sample similarly. For the blank take about 126 mg lithium fluoride.

2. Irradiate for 30 minutes in the Harwell Pile (at normal power). Meanwhile assemble the distillation apparatus.
3. Transfer as much as possible of the contents of each tube to separate distillation flasks which already contain about 0.25 g glasswool and 0.5 g silver sulphate, plus a few ml of water. Add 60 ml of 50% v/v sulphuric acid and immediately insert the thermometer.
4. After initial evolution of hydrogen heat the flask until the temperature reaches 130°-135° C; pass in steam and collect about 200 ml of distillate at a rate of 4-5 ml per minute with the temperature generally between 140° and 150°, with an upper limit of 155°.
5. Heat the distillate to boiling in a beaker and add 2 drops 10% sodium chloride solution, followed by 10 drops 10% silver nitrate solution. Boil for a few minutes and filter twice through a sintered glass crucible No. 4. Reheat filtrate and add 3-4 ml 10% sodium chloride, boil and filter twice. Cool the liquid.
6. Add 2 drops of 0.4% bromophenol blue and 3 ml of 10% (w/v) sodium chloride solution. Adjust the pH by adding $2N$ sodium hydroxide until the solution just turns blue. Add 1 ml conc. hydrochloric acid and 5 grams solid lead nitrate; heat the solution to about 70° C and add 5 g sodium acetate trihydrate, stirring vigorously for one minute. Set aside for a few minutes and re-stir. Add a few drops of 0.2% aqueous solution of aerosol and set aside to cool for about 20 minutes. a)
7. Decant the majority of the supernate and transfer the remainder and precipitate to a 40 ml centrifuge tube. Add 2 drops of aerosol and centrifuge for 2 minutes. Decant, wash and centrifuge the precipitate successively with saturated lead chlorofluoride solution, water and twice with acetone. b)
8. Slurry the majority of the precipitate on to a weighed aluminium tray using acetone and a transfer pipette. Dry on hotplate, finally at about 250° C for a few minutes, cool and weigh.
9. Measure the β activity at constant counting efficiency, using a normal G.M. end window arrangement, at various times after the end of irradiation.

Method of calculation

1. Plot the activities measured at various times after irradiation as a decay curve and check that the half life is 112 ± 2 min. Hence obtain the activity at 240 minutes from the end of the irradiation.
2. Apply a correction for chemical yield to give the activity corresponding to 126 mg lithium fluoride, that is, 92.3 mg fluorine (factor for F from LiF is 0.7324 and from PbClF is 0.0726).

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a) The time of standing of precipitate is the chief factor governing the final yield; times shorter than 15 minutes are liable to result in yields of less than 50%.

b) Use about 35 ml aqueous washing solution, and 15 ml acetone. It is very important to stir well to wash all the precipitate—otherwise acid is occluded and attacks the aluminium counting tray.

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3. Apply a correction for β self-absorption to give the activity which would be apparent in a 1 gram source.
4. From the activities so obtained for the "blank", standard and sample calculate the oxygen content.

Preparation of β self-absorption correction-graph

1. Irradiate for about 30 minutes a known amount (approximately 35 mg) of a mixture of lithium fluoride and beryllium oxide in a ratio of about 1.3 : 1. Distil about 200 ml, "scavenge" with silver salt and make up to 250 ml. This is the "active solution".
2. Simultaneously distil the fluorine from about 1.1 grams of inactive lithium fluoride. Collect approximately 400 ml and make up to 500 ml.
3. Prepare mixtures each containing 25 ml of active solution, plus varying volumes of inactive solution — 30, 36, 42, 48, 54, 60, 66 and 72 ml. Make each solution up to 100 ml.
4. Precipitate, mount and weigh the lead chlorofluoride by the usual method and measure the β activities at a constant counting efficiency. Check the half life of the "active solution" and if satisfactory calculate the activity for each source at one particular time using 112 minutes as the value of the ^{18}F half life.
5. Apply corrections for the chemical yield. The theoretical yield is obtained as the sum of the yields expected for the active and inactive solutions. The former may be calculated directly from the weight of lithium fluoride irradiated, the small loss involved in distillation being negligible compared with the final weights of the sources. For the inactive solution the fluorine is estimated by lead chlorofluoride precipitation on 25 ml samples. In these cases the precipitate is allowed to stand overnight to give 100% recovery.
6. The corrected activities are plotted as a function of the experimental weights of the sources. They represent the activities given by a constant activity when contained in different weights of lead chlorofluoride, and the required correction factors are obtained by comparing the various activities with that given for a 1 gram source.

Note

The quantities quoted above afford sources of weight between 0.6 and 1.5 grams. For wider ranges the volumes taken in stage 3 are suitably adjusted.

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SUMMARY

A radioactivation method for the determination of oxygen in beryllium metal powder is described. The sample, mixed with lithium fluoride, is irradiated in the Harwell Pile, fluorine-18 chemically separated and its activity compared with that from standards similarly treated.

The method has given reproducible results in reasonable agreement with those obtained by several other methods which were being investigated simultaneously.

RÉSUMÉ

Les auteurs décrivent une méthode radioactive pour le dosage de l'oxygène dans le béryllium métallique pulvérulent. L'échantillon, mélangé au fluorure de lithium est irradié par la pile Harwell; le fluor-18 est séparé chimiquement et son activité est comparée à celle d'étalons traités de la même façon. Cette méthode donne des résultats reproductibles, correspondant à ceux obtenus par d'autres méthodes utilisées parallèlement.

ZUSAMMENFASSUNG

Es wird eine radioaktive Methode zur Bestimmung von Sauerstoff in Berylliummetallpulver beschrieben. Die mit Lithiumfluorid vermischte Probe wird im Harwell-Pile bestrahlt, Fluor-18 chemisch abgetrennt und seine Aktivität verglichen mit der von ähnlich behandelten bekannten Proben.

Die Methode ergab reproduzierbare Werte, die gut mit denen von mehreren anderen gleichzeitig untersuchten Methoden übereinstimmen.

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REACTION OF IRON(II) WITH 1,2-CYCLOHEXANEDIONEDIOXIME IN ACID SOLUTION

by

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INTRODUCTION

Since the discovery of the reaction between nickel and 2,3-butanedionedioxime (dimethylglyoxime) by TSCHUGAEFF[10] in 1905, the *vic*-dioximes have been used for the detection and gravimetric determination of nickel. In recent years, the water-soluble dioximes, especially 1,2-cyclohexanedionedioxime (nioxime) and 1,2-cycloheptanedionedioxime (heptoxime), have become important reagents for nickel. Nickel can be determined gravimetrically in the presence of iron with 2,3-butanedionedioxime or 1,2-cycloheptanedionedioxime if Fe(III) is masked with tartrate or citrate[1,13]. However, when 1,2-cyclohexanedionedioxime is used as a precipitant for nickel, the iron interference cannot be eliminated by adding tartrate or citrate. High or low results are obtained depending on the pH conditions of the precipitation[2,12].

The red-violet, soluble complexes of Fe(II) with the *vic*-dioximes in the presence of ammonia and a variety of amines have been extensively investigated[1,4,7]. While working in non-ammonical, slightly acid solution, FERGUSON AND BANKS observed that in the presence of 1,2-cyclohexanedionedioxime, Fe(II) forms a brown solution having a spectrum significantly different from that of an Fe(II)-amine-*vic*-dioxime complex[3]. Furthermore, they reported that 1,2-cyclohexanedionedioxime reduces Fe(III), then complexes the resulting Fe(II). The reaction of Fe(II) with 1,2-cyclohexanedionedioxime has been studied to learn the nature of the iron interference in the determination of nickel.

APPARATUS

Absorption spectra were automatically recorded by a Cary spectrophotometer, Model 12, at a slit control setting of 10. A Beckman spectrophotometer, Model DU, was used for the determination of iron by the 1,10-phenanthroline method.

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* Work was performed in the Ames Laboratory of the Atomic Energy Commission.

Matched corex or silica cuvettes were used in all spectrophotometric work.

All pH measurements were made with a Beckman pH meter, model G. Commercial buffers were used to standardize the instrument.

Small pipets and all burets, except those used for the Karl Fischer titration, were "Normax" brand glassware. Volumetric flasks and larger pipets were "Normax", "Exax", or "Pyrex" brand glassware.

REAGENTS

Iron(II) sulfate, $FeSO_4.7H_2O$, reagent special, containing less than 0.01% Fe(III), was used. Since Fe(II) solutions in 1 *N* acid are not stable for long periods, they were made as they were needed. Solutions were standardized titrimetrically with a standard Ce(IV) solution or spectrophotometrically with 1,10-phenanthroline. Iron(III) ammonium sulfate, $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, containing less than 0.001% Fe(II) was used. A stock solution was made by dissolving the salt in 2*N* sulfuric acid and was standardized titrimetrically with standard cerium(IV) solution after reduction in a Jones reductor.

1,2-Cyclohexanedionedioxime was prepared in these laboratories according to the procedure of HACH, BANKS AND DIEHL[9]. Stock solutions were standardized by adding an excess of Ni(II) sulfate solution to ammonium acetate buffered aliquots, then digesting, filtering, drying and weighing the insoluble bis (1,2-cyclohexanedionedioximato-*N*, *N'*)nickel(II).

Sodium acetate-acetic acid buffer was made by dissolving 130 grams of reagent grade sodium acetate, $NaC_2H_3O_2.3H_2O$ in water, adding 30 ml of glacial acetic acid and diluting to 500 ml in a volumetric flask. This solution contains about 2 moles of sodium acetate and 1 mole of acetic acid per liter of solution. Thus, constant ionic strength (0.25) and constant pH (4.82 ± 0.02) were maintained.

Prepurified nitrogen that had been passed through an alkaline pyrogallol solution to remove the last traces of oxygen was kept over Fe(II) solutions to minimize air oxidation. All other chemicals used were the best available reagent grade and were low in iron, nickel and cobalt. Deionized, distilled water was used in making all solutions.

EXPERIMENTAL PROCEDURES AND RESULTS

1,2-Cyclohexanedionedioxime in acid solutions. Hydrogen ion is liberated in the reaction of Fe(II) with 1,2-cyclohexanedionedioxime. To eliminate the pH variable it is necessary to use a buffer or to work at sufficiently high hydrogen ion concentration that the contribution of additional hydrogen ion by the reaction is negligible. Although the nickel determination is usually made from acetate buffered solution[12], Fe(II) in solution is less readily air oxidized at higher hydrogen ion concentrations. The stability of 1,2-cyclohexanedionedioxime in 0.1*N* acid solution and in sodium acetate-acetic acid buffered solution (pH 4.8) was investigated spectrophotometrically.

The ultraviolet absorption spectrum of 1,2-cyclohexanedionedioxime in 0.1N sulfuric, nitric, hydrochloric or perchloric acid (a broad maximum at 300 mμ and a sharp maximum at 239 mμ) is different from its spectrum in neutral solution (a broad maximum at 232 mμ). This change in the spectrum of the reagent takes place slowly. Although the changed spectrum is evident after one day, the absorbances of the maxima continue to increase for at least a week. The characteristic spectrum of the acid solution is not changed when an acid solution is neutralized or made basic. It is probable that a decomposition product rather than a protonated reagent molecule is responsible for the spectrum of an acid solution of the reagent. The absorbing species has not been identified; however, its spectrum does not resemble that of 1,2-cyclohexanedione, 2-hydroxyiminocyclohexanone or 1,2-cyclohexanediamine hydrochloride in acid solution.

The absorption spectrum of 1,2-cyclohexanedionedioxime in the presence of acetate above pH 3 is the sum of the individual spectra of the reagent and acetate, and it does not change with time. Therefore, the reaction of Fe(II) with 1,2-cyclohexanedionedioxime was studied in acetate buffered solution, the medium recommended for the determination of nickel with the same reagent [12]. Several spectrophotometric determinations of Fe(II), notably that with 1,10-phenanthroline, are carried out in acetate buffered solution. Acetate complexes Fe(III) but does not complex Fe(II) appreciably. The spectrum of Fe(III) in acetate solution is shown in Fig. 3.

Complex in solution. The visible absorption spectrum of the complex has a maximum absorbance at 464 mμ and a minimum absorbance at about 390 mμ. Iron(II) and 1,2-cyclohexanedionedioxime as well as the complex absorb in the ultraviolet region and an absorbance maximum has not been observed for the complex in that region. The amount of complex formed varies inversely with the initial hydrogen ion concentration (Table I and Fig. 1). The appearance of a plateau instead of a peak in the absorption spectrum of the solution at a high pH (Fig. 1, curve 5) is thought to be due to turbidity resulting from the oxidation of Fe(II) and its subsequent hydrolysis.

TABLE I

SOLUTIONS USED TO ILLUSTRATE THE pH DEPENDENCE OF COMPLEX FORMATION*

Solution number	ml 1N $HClO_4$	ml 1N NaOH	pH
1	30	0	2.08
2	15	0	4.02
3	0	0	4.68
4	0	15	5.05
5	0	30	8.62

* All solutions are $7.50\cdot10^{-5}M$ in Fe(II), $1.75\cdot10^{-4}M$ in 1,2-cyclohexanedionedioxime, and contain 25 ml of buffer solution in 200 ml total volume.

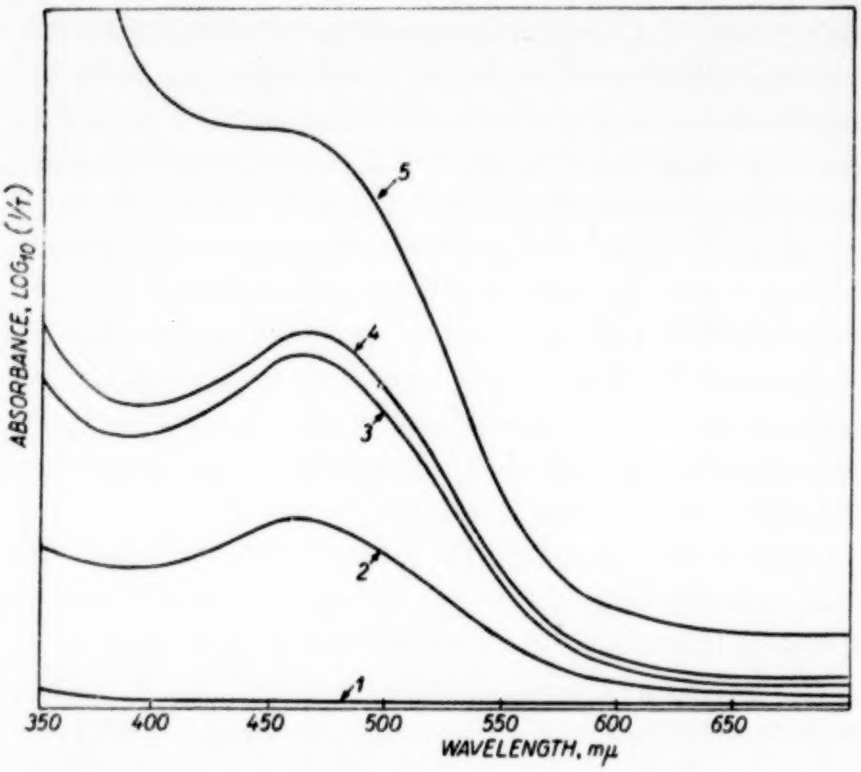

Fig. 1. Absorption spectra of complex at several pH's.

Numbers correspond to solutions described in Table I.

Scanned in 5.0 cm cuvettes vs. distilled water.

The complex forms slowly. The increase in absorbance at the maximum as a function of time is shown in Fig. 2. Equilibrium is not attained even after three

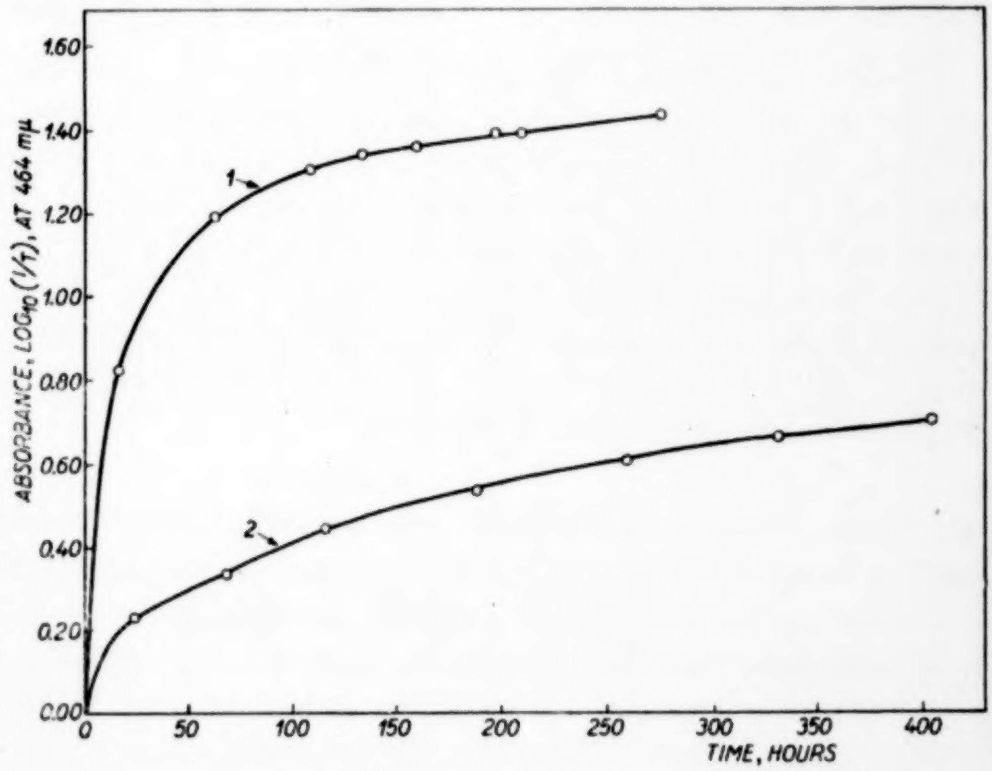

Fig. 2. Effect of time on absorbance of Fe(II)-1,2-cyclohexanedionedioxime and Fe(III)-1,2-cyclohexanedionedioxime solutions. 5 cm cuvettes vs. distilled water.

Curve 1: $1.50 \cdot 10^{-4} M$ Fe(II), $1.50 \cdot 10^{-4} M$ 1,2-cyclohexanedionedioxime, 25 ml sodium acetate-acetic acid buffer in 200 ml total volume, stored under nitrogen.

Curve 2: $1.50 \cdot 10^{-4} M$ Fe(III), $1.50 \cdot 10^{-4} M$ 1,2-cyclohexanedionedioxime, 25 ml sodium acetate-acetic acid buffer in 200 ml total volume.

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weeks. The slow complex-forming reaction is especially disadvantageous because Fe(II) in solution is readily air oxidized above pH 3. No suitable reducing agent for Fe(II) has been found for this reaction. When hydroxylammonium chloride was used, a new maximum began to appear after a week at 568 mμ. Sodium sulfite (Na_2SO_3), sodium thiosulfate ($Na_2S_2O_3$), granular zinc, and aluminum hindered the complex formation. Therefore, all solutions containing Fe(II) were stored under nitrogen. As can be seen in curve 2, Fig. 3, this precaution did not eliminate oxidation of Fe(II), since some Fe(III)-acetate is formed, but certainly minimized it.

The central atom in the complex is thought to be Fe(II) rather than Fe(III). The absorption spectra of a Fe(II)-1,2-cyclohexanedionedioxime solution and a Fe(III)-1,2-cyclohexanedionedioxime solution approximately the same length of time after preparation are shown in Fig. 3. If the absorption spectrum of

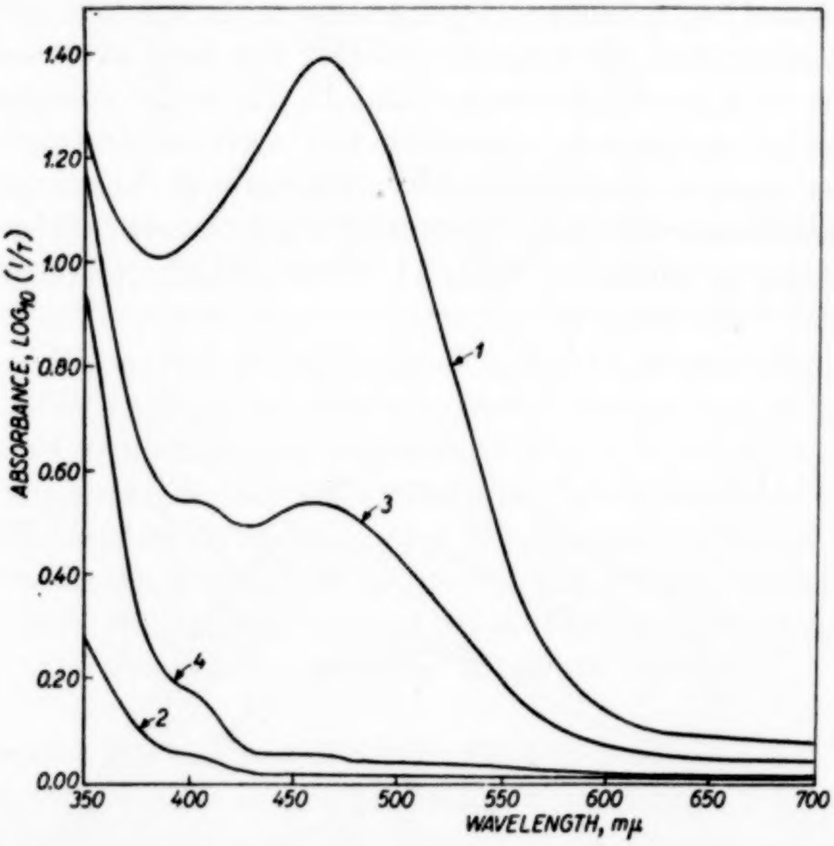

Fig. 3. Absorption spectra of Fe(II)-1,2-cyclohexanedionedioxime and Fe(III)-1,2-cyclohexanedionedioxime solutions of same concentration at comparable time. (Scanned in 5 cm cuvettes vs. distilled water)
Curve 1: $1.50 \cdot 10^{-4} M$ Fe(II), $1.50 \cdot 10^{-4} M$ 1,2-cyclohexanedionedioxime, 25 ml sodium acetate-acetic acid buffer in 200 ml total volume, stored under nitrogen, at 197.3 hours.
Curve 2: $1.50 \cdot 10^{-4} M$ Fe(II), 25 ml sodium acetate-acetic acid buffer in 200 ml total volume, stored under nitrogen, at 197.3 hours.
Curve 3: $1.50 \cdot 10^{-4} M$ Fe(III), $1.50 \cdot 10^{-4} M$ 1,2 cyclohexanedionedioxime, 25 ml sodium acetate-acetic acid buffer in 200 ml total volume, at 189.0 hours.
Curve 4: $1.50 \cdot 10^{-4} M$ Fe(III), 25 ml sodium acetate-acetic acid buffer in 200 ml total volume, at 189.0 hours.

Fe(III)-acetate is taken into account, the curves are of the same form, indicating that the same complex exists in both solutions. It can be seen in Fig. 2 that in the Fe(III) solutions not only is the complex formed more slowly than in the Fe(II) solutions, less of it is formed. Therefore, it seems probable that the central atom in the complex is Fe(II) and that in Fe(III) solutions some Fe(III) is reduced, probably by 1,2-cyclohexanedionedioxime and then forms the complex.

The color of the complex can be discharged by adding an excess of oxidizing agent. After the color of the complex is destroyed by cerium(IV) or potassium metaperiodate, addition of Ni(II) followed by digestion of the solution results in the formation of the characteristic red precipitate, which shows that the 1,2-cyclohexanedionedioxime has not been completely destroyed. Iron(II) is probably oxidized to Fe(III), and thus destroys the complex. The color of the complex can also be destroyed by prolonged heating with sodium sulfite. However, upon the addition of Ni(II) followed by digestion of the solution, no red precipitate is formed, indicating that the reagent probably has been attacked. These qualitative experiments support the theory that Fe(II) is the complex-forming ion.

Job's method of continuous variations was used to determine the ratio of ligand to central atom in the complex [5,6,11]. The ratio of the concentration of one component in solution to the other was varied while the sum of the concentrations was held constant, as shown in Table II. Since neither component absorbs ap-

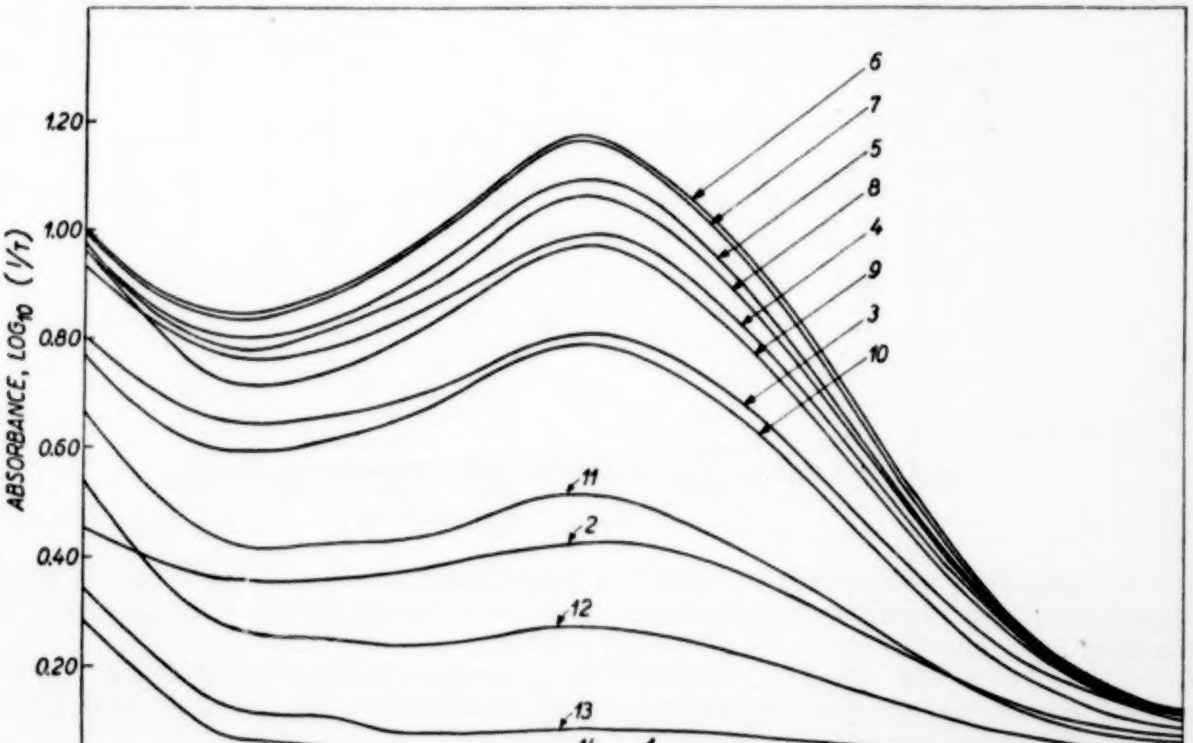

Fig. 4. Absorption spectra of Job's solutions of complex. Scanned in 5 cm cuvettes vs. distilled water. Numbers correspond to solutions described in Table II. Eight days after preparation.

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TABLE II

SOLUTIONS USED FOR ANALYSIS BY JOB'S METHOD*

Solution number	N Fe(II) x 10^4	N 1,2-Cyclohexanedionedioxime x 10^4
1	0	2.50
2	0.25	2.25
3	0.50	2.00
4	0.63	1.88
5	0.75	1.75
6	0.88	1.63
7	1.01	1.50
8	1.13	1.38
9	1.26	1.25
10	1.51	1.00
11	1.76	0.75
12	2.01	0.50
13	2.26	0.25
14	2.52	0

* All solutions contain 25 ml of buffer solution and 10 ml of 1 N $NaClO_4$ in a total volume of 200 ml, giving an ionic strength of 0.30.

preciably in the visible (Fig. 4), the ratio of ligand to central atom can be determined directly from a plot of absorbance against composition (Fig. 5). In Fig. 5 it is indicated that in the complex two molecules of 1,2-cyclohexanedionedioxime are associated with each Fe(II) ion. Several similar series were made and were analyzed at different periods of time after preparation. Although the individual spectra varied with time, the plot of absorbance against composition always gave the same ratio of ligand to central atom. Precipitation in the presence of excess reagent was avoided by working in dilute solution.

Solid compound. A black, finely divided solid is formed when a large amount of 1,2-cyclohexanedionedioxime in acetate buffered solution is added to an Fe(II) solution of a concentration of $10^{-4}M$ or greater. The vacuum-dried compound is not soluble in acetone, benzene, carbon tetrachloride, diethyl ether or glycerol. It is quite soluble in pyridine, ammonium hydroxide and concentrated acids and is less soluble in methanol, ethanol and ethylene glycol. The vacuum-dried solid is slightly soluble in cold water in which it dissolves slowly with no change in pH. The absorption spectrum of the water solution qualitatively resembles that of the soluble complex.

The solid compound decomposes when dried in an oven at 105° C. The vacuum-dried solid is hygroscopic. During the first half-hour of its exposure to the atmosphere, a vacuum-dried sample weighing 0.4 g was found to gain weight at the

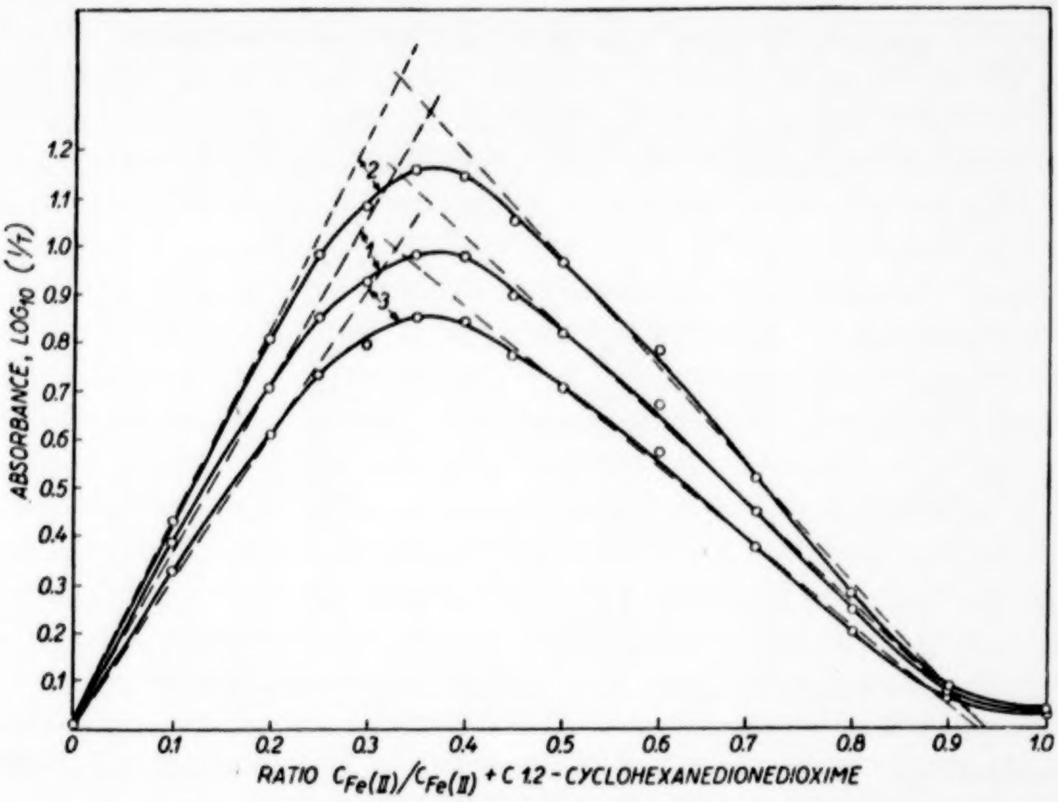

Fig. 5. Determination of ratio of ligand to central atom by JOB's method.
Curve 1: at 430 mμ.
Curve 2: at 464 mμ.
Curve 3: at 510 mμ.

rate of 0.00011 g/min. The amount of moisture gained by the sample seemed to vary within a range, and the sample did not attain constant weight.

The following procedure was used for making the solid compound. One hundred ml of 0.05*M* 1,2-cyclohexanedionedioxime (5.0 millimoles) and 20 ml of buffer solution were measured into a beaker. Approximately 0.15 g of iron(II) sulfate, $FeSO_4 \cdot 7H_2O$ (0.5 millimoles), was weighed into a small beaker and dissolved in a minimum amount of water containing sulfuric acid. The solutions were mixed, and formation of the precipitate was immediate. The solution was digested, and the precipitate was allowed to settle. The solid was transferred to centrifuge tubes, washed several times with portions of hot water, and air-dried. It was transferred to an open weighing bottle and dried in a vacuum desiccator for several days until the solid attained constant weight.

The iron content of the solid was determined spectrophotometrically with 1,10-phenanthroline. Each sample was dissolved by heating with a mixture of nitric and hydrochloric acids. Analysis of seven vacuum-dried samples showed the iron content of the solid compound to be 15.28 ± 0.13%. The amount of 1,2-cyclohexanedionedioxime in the solid compound was established from the nitrogen content of the material determined by the micro Dumas method. Analyses of

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four vacuum-dried samples of the solid showed its nitrogen content to be 14.88 ± 0.09%. Water was removed from the solid compound by an azeotropic distillation and was determined by a Karl Fischer titration[8]. Analysis of two samples gave the results 10.7% and 11.2% of H_2O. The analysis of the solid compound is in agreement with the composition of the solid $Fe(DH)_2.2H_2O$*: 14.93% Fe, 14.97% N, 9.63% H_2O.

DISCUSSION

Analysis of the solid compound and of the complex in solution has shown that two molecules of 1,2-cyclohexanedionedioxime are associated with each Fe(II). The absorption spectra of the soluble complex and a solution of the solid compound are similar. The ratio of 1,2-cyclohexanedionedioxime to iron is the same in the soluble and solid complexes, and, since the hydrogen ion concentration of the solvent is not changed when the solid is dissolved in water, it is possible that the relationship between the complex in solution and the solid compound is one of solubility.

The study of the reaction of Fe(II) with 1,2-cyclohexanedionedioxime has not led to any new ideas for the elimination of the iron interference in the determination of Ni(II) with this reagent. Small amounts of iron should not interfere seriously. Large amounts of iron should probably be removed by extraction before the nickel determination is carried out. FEINSTEIN[2] reported slightly high results in the determination of nickel in steel with 1,2-cyclohexanedionedioxime in tartrate solutions. A reprecipitation was necessary. 1,2-Cycloheptanedionedioxime is a superior reagent for nickel, and iron causes no interference when complexed with tartrate.

SUMMARY

Information about a decomposition of 1,2-cyclohexanedionedioxime in 0.1 *N* acid has been presented. A spectrophotometric study of the reaction of Fe(II) with 1,2-cyclohexanedionedioxime in dilute, acetate buffered solutions containing no ammonia or amine has been reported. The ratio of 1,2-cyclohexanedionedioxime to Fe(II) was found to be 2:1 by JOB's method. The solid compound formed when an excess of 1,2-cyclohexanedionedioxime is added to more concentrated Fe(II) solutions has been studied. Analysis of the vacuum-dried solid is in agreement with the theoretical composition of the compound $Fe(DH)_2.2H_2O$.

RÉSUMÉ

Des renseignements sont donnés au sujet de la décomposition de la 1,2-cyclohexanedionedioxime en solution acide 0.1 *N*. Les auteurs ont effectué une étude spectrophotométrique de la réaction Fe(II)-1,2-cyclohexanedionedioxime, en solutions diluées et tamponnées à l'acétate, en l'absence d'ammoniaque ou d'amines. Le rapport de 2:1 entre la 1,2-cyclohexanedionedioxime et le fer(II), a été déterminé par la méthode de JOB. Le composé solide formé lors de la précipitation de Fe(II), en solution plus concentrée, par un excès de 1,2-cyclohexanedionedioxime a été étudié. L'analyse du composé séché au vide correspond à la composition théorique du composé $Fe(DH)_2.2H_2O$.

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* DH_2 represents the neutral reagent molecule; DH^- and D^{-2} represent the ionized species.

ZUSAMMENFASSUNG

Es wurde über die Zersetzung des 1,2-Cyclohexandiondioxims in 0.1*N* Säure und eine spektrophotometrische Untersuchung der Reaktion von Fe(II) mit 1,2-Cyclohexandiondioxim in verdünnten mit Acetat gepufferten und weder Ammoniak noch Amin enthaltenden Lösungen berichtet. Das nach der Methode von JOB gefundene Verhältnis von 1,2-Cyclohexandiondioxim zu Fe (II) betrug 2:1. Die durch Hinzufügen eines Überschusses von 1,2-Cyclohexandiondioxim zu konzentrierteren Fe(II)-Lösungen gebildete feste Verbindung wurde untersucht. Die Analyse des im Vakuum getrockneten festen Körpers stimmt mit der theoretischen Zusammensetzung von $Fe(DH)_2 \cdot 2H_2O$ überein.

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ALKYL SUBSTITUTED 2,2'-DIQUINOLINES AND ALTERATION OF THEIR SPECTROPHOTOMETRIC CONSTANTS FOLLOWING COPPER(I) CHELATION

by

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INTRODUCTION

Cuproine (2,2'-diquinoline) was originally studied by BRECKENRIDGE, LEWIS AND QUICK[1] for use in the spectrophotometric determination of copper. The experimental work by HOSTE[2], and by BRECKENRIDGE[3] included, together with other material, the study of methyl-substituted diquinolines and the resultant alteration in the spectrophotometric constants of their Cu(I) complex cations.

HOSTE[2] was the first to observe that the chelate formed by cuproine with Cu(I) is extractable from aqueous solutions through the use of an immiscible solvent. This development greatly improves the sensitivity of these types of heterocyclic ring nitrogen compounds as chelating reagents. The Cu(I) complex cations of 2,2'-dipyridine and 1,10-phenanthroline were thought to be unextractable using immiscible solvents, but it has been demonstrated that extraction is possible provided their alkyl substituted homologues are used.

(Cuproine may be considered as a benzinoid alkylation of 2,2'-dipyridine.) Advantage has been taken of this procedure in the case of the Cu(I) complex cations of substituted 1,10-phenanthrolines[4,5] and the iron and cobalt complexes of 2,2',2''-terpyridines, terosine and terosole[6], which are 4-alkyl substitutes of 2,2',2''-terpyridine. Recently it has been shown that the Cu(I) complex with 1,10-phenanthroline may be extracted provided a higher molecular weight alcohol, such as *n*-hexyl or *n*-octyl alcohol, is used[7].

In the spectrophotometric determination of copper, the research objective involves, primarily, a group of three goals, namely, (1) improved specificity (2) increased sensitivity and, (3) manipulative simplification. The three type ligands last cited have as chemically similar functional groups, the ferroine, the cuproine and the terroine groups. As a result they are also similar in showing a high degree of specificity in cases involving their Cu(I), and in some cases their

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*Recipient of the Fifth Annual Merck Graduate Fellowship in Analytical Chemistry.

Fe(II) and Co(II), chelated complex cations. These alone involve color in the visible spectral range. Moreover, extraction by immiscible solvents increases this non-interference from the presence of other colored ions which are not similarly extracted. Manipulative simplicity is contributed in no small degree owing to the fact that the colored complex cations of these type ligands are formed over a wide range of pH values and are stable under storage for ordinary laboratory conditions over an even wider range of pH values for long periods of time. In addition, means may be readily applied to avoid the mutual interference of iron in the determination of copper or copper in the determination of iron, thus providing increased specificity.

The remaining research objective is that of improving sensitivity. This objective is attained, as has been proven in a study of a large number of substituted 1,10-phenanthrolines[8,9] as Fe(II) and Cu(I) complex cations, by altering structure. This includes predictable alterations in the redox potential of the $Fe^{+3} + e^{-} = Fe^{+2}$ single electrode potential of their iron complexes and in the molecular extinction coefficient of the colored complex in question as well as alteration of the wavelength of maximum absorption to a predictable magnitude.

The present discussion involves the study of ten mono- and dialkyl substituted 2,2′-diquinolines and the resultant modification in the spectrophotometric constants of their Cu(I) complex cations. An attempt is made to gain an understanding of possible property prognoses. These result from selective structural alterations following alkyl substitutions in the molecule outside the configuration of the specific functional group.

REAGENTS STUDIED

The 2,2′-diquinoline (cuproine) and mono- and di-substituted 3,4, and 4,4′-substituted diquinolines included are listed as samples number 1 to number 10 inclusive in Table I. BRECKENRIDGE[3] gives some data for 4,4′-dimethyl-2,2′-diquinoline herein included (number 9 in Table I).

PREPARATION OF REAGENTS

Materials will be referred to with identification according to numbers taken from Table I.

1. From quinoline as described by BRECKENRIDGE, LEWIS AND QUICK[1] using ferric chloride in a dehydrogenation under pressure of quinoline at 325° C. It may also be prepared as described by HOSTE[2] employing the Friedlander synthesis in the coupling of quinolylmethylketone with *o*-aminobenzaldehyde, m.p. 196°.
2. Friedlander synthesis employing quinolylethylketone and *o*-aminobenzaldehyde as described by HOSTE[2], m.p. 136°.

3 to 8 inclusive. These preparations were synthesized by Professor FRANCIS CASE of Temple University by procedures to be described in data for subsequent publication[10].

9. Prepared as described by BRECKENRIDGE[2] and duplicating the reaction employed for the preparation of 1 but employing 4-methyl quinoline in place of unsubstituted quinoline, m.p. 280-281°; this preparation was submitted by Professor FRANCIS CASE.

10. Prepared by a method to be subsequently reported by Professor FRANCIS CASE.

TABLE I

SUBSTITUTED 2,2′-DIQUINOLINE DERIVATIVES, PHYSICAL CONSTANTS OF THEIR COPPER(I) COMPLEX CATIONS

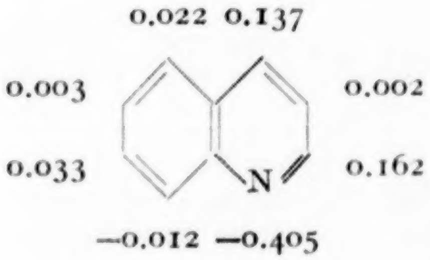
Compound number and type	Molecular extinction coefficient of Cu(I) complex cation	Wavelength max. absorption in mu of Cu(I) complex	
		Maximum	Minimum
(1) 2-2′-Diquinoline	5490	540	430
(2) 3-Methyl-2,2′-Diquinoline	4120	520	435
(3) 3-Ethyl- ,, ,,	3030	525	438
(4) 3-Propyl- ,, ,,	3500	523	438
(5) 3-Phenyl- ,, ,,	5610	529	434
(6) 3-Carbethoxy- ,, ,,	3420	519	435
(7) 4-Methyl- ,, ,,	6590	547	428
(8) 4-Phenyl- ,, ,,	8440	553	432
(9) 4,4′-Dimethyl- ,, ,,	7140	551	431
(10) 4,4′-Diphenyl- ,, ,,	9020	559	440

STRUCTURAL MODIFICATIONS AND RESULTANT PROPERTY ALTERATIONS

From an examination of the data of Table I the most striking conclusion observable is the relationship made evident associating the wavelength of maximum absorption with the molecular extinction coefficient of the Cu(I) complex. An increase in wavelength of maximum absorption of the substituted ligand as the Cu(I) chelate is always accompanied by an increase in the value of the molecular extinction coefficient. The opposite is true for a decrease in the wavelength of maximum absorption. The magnitudes of the two alterations are proportional.

The instability constant of the Cu(I) complex cation, which dissociate giving copper ions and ligand molecules, can be postulated safely as being inversely proportional to the increase in molecular extinction coefficient. Under this assumption, substitutions in the 3 position (and almost certainly, likewise, in the case of diquinolines having alkyl substitutions not included in the compounds studied) affect adversely the coplanarity of the molecular configuration of the ligand. This distortion of the molecular configuration of the ligand increases the distance between the nitrogen atoms in the functional group R-C=N-C-C-N=C-R. (Strangely, the 3-phenyl substitution constitutes an exception to this rule.) The reason this is true becomes apparent through considerations involving the electron density distribution in the quinoline molecule.

This electronic structure has been calculated by LONGUET-HIGGINS AND COULSON[11] indicating the following values:



Modifications in this electronic structure following coupling in the 2 and 2′-positions to form 2,2′-diquinoline have not been calculated, but it may be reasoned by analogy with the known electronic configuration already calculated[11] for 1,10-phenanthroline. The electron surplus associated with the nitrogen of diquinoline will be only little altered. The corresponding increase in the electron deficiency in the 4,4′-positions of hydrogen in diquinoline due to coupling in the 2,2′-position is not known. However, the electron deficiency in the 4,4′-positions may be predicted to increase as the result of the coupling.

The substitution of alkyl groups in the 3,3′-positions in diquinoline would be predicted to alter the tendency to modify the molecular extinction coefficient as a result of two opposite effects. The first of these is the effect of distortion of the ligand structure out of coplanarity. The other is the increase in electron deficiency around the nitrogen atoms of the specific functional group which increases the basicity. Distortions resulting in a deficiency in coplanarity diminish the molecular extinction coefficient. The augmentation of the electron density at the nitrogen atoms increase the molecular extinction coefficient.

The substitution of the methyl, ethyl, N-propyl, and carbethoxy groups in the 3 position (and presumably in the 3,3′-positions, if involved) lower the wavelength of maximum absorption accompanied by a corresponding decrease in the molecular extinction coefficient. The conclusion must, therefore, be drawn that the distortion resulting in non-coplanarity is greater in effect than the electron donation by these groups in tendency to increase these values in magnitude through electronic alterations in structure.

The effect is the opposite when the phenyl group is substituted for the 3 hydrogen position of diquinoline. The wavelength of maximum absorption decreases from 540 mμ to 529 mμ but the molecular extinction coefficient increases from 5490 to 5610. These alterations in effects are due to the fact that the phenyl group is a better electron donor than the methyl group and this increased influence offsets the predicted distortion effect in coplanarity in the ligand molecule.

As is so obvious in connection with the substitutions of the methyl or, to a greater extent, the phenyl group, in the case of the 4,7′-positioned hydrogen in 1,10-phenanthroline these same 4,4′-positions in the diquinoline ligand provide maximum alteration in properties. The increase in both the wavelength of maximum absorption and in the molecular extinction coefficient of the Cu(I) chelate is at once apparent. The effect is more pronounced in the case of phenyl substitutions than methyl substitution. Likewise, the substitution of these alkyl groups in the 4,4′-position results in increased alterations over the single substitutions. Here the effects would be predicted to result as stated owing to the excess of electron donor effects uncomplicated by steric hindrance effects comparable with that resulting from similar substitutions in the 3,3′-positions of the ligand.

From these conclusions it is obvious that any further attempts to modify the molecular structure of diquinoline favorably should involve only substitutions of special groups in the 4,4′-positions. The particular group substitution should involve only ones which are better electron donors than the phenyl group.

The superiority in selectivity and sensitivity of modified 1,10-phenanthrolines as influenced by alkyl and other group substitutions in the 4,7-positions and in the 2,9-positions or the 2, 4, 7, 9-positions, it would appear certain, will always be realized to a greater extent than similar substitutions in the diquinolines in the 4,4′-positions. This is primarily true because with 1,10-phenanthroline the situation regarding coplanarity of the molecular structure is fixed while with diquinoline lack of coplanarity is to a greater or less extent always a complicating influence.

The objective in the compilation of the present data consists in an attempt to supply experimental data and interpretation leading to a better understanding of the structural modification of organic molecules resulting in property prognosis in the remarkable series of ligands containing the ferroine, cuproine and terroine functional groups. A successful effort in this program may, with continued study, through the combined efforts of the synthetic organic chemist in synthesis, the physical chemist in determination of physical constants, and the research analyst in developing procedures in their application, point to almost definitely certain advancements, with less unfortuitous speculative efforts associated with an unsystematic study otherwise necessitated. There then remains the still obvious necessity for the consumer to interest a manufacturer in making the preferred reagents commercially available.

GRAPHICAL RECORDING OF SPECTROPHOTOMETRIC CHARACTERISTICS

The spectrophotometric curves from a series of observations of the Cu(I) complexes are given in the case of 4-phenyl-2,2′-diquinoline in Fig. 1. Duplicate recordings for the same complex employing 4,4′-diphenyl-2,2′-diquinoline as ligand are shown in Fig. 2. These ligands result in the formation of Cu(I) complex cations which have the highest value molecular extinction coefficients yet found in the 2,2′-diquinoline series, 8440 and 9020. Both these colored complexes are

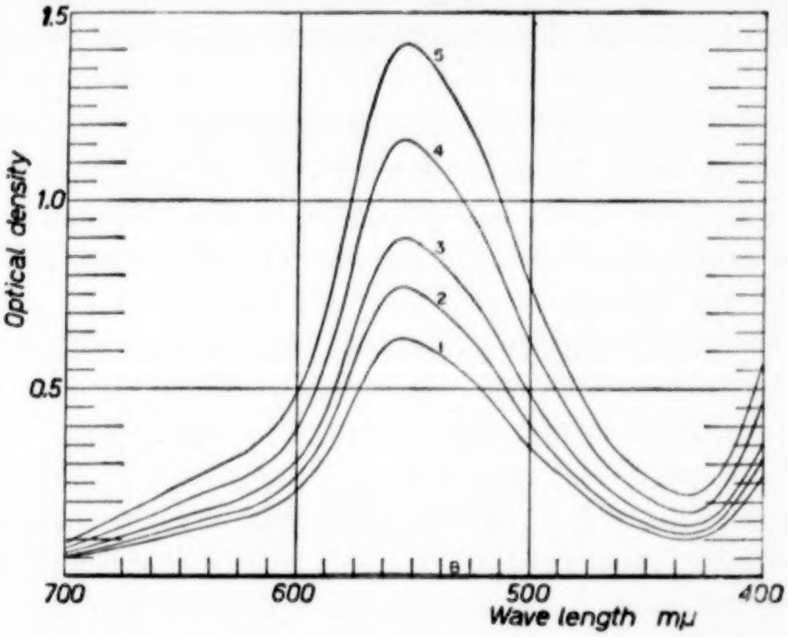


Fig. 1. 4-Phenyl-2,2′-diquinoline Cu+ complex.

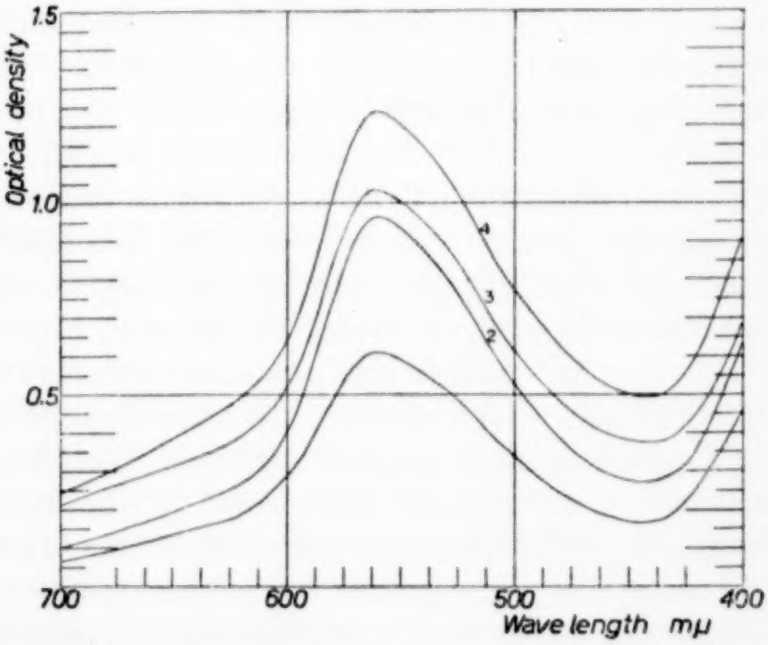


Fig. 2. 4,4′-Diphenyl-2,2′-diquinoline Cu+ complex.

extractable from aqueous solution employing a number of water immiscible organic solvents. These ligands show no greater specificity than 2,9-dimethyl-1,10-phenanthroline[4] or lessertendency towards complete extractability employing immiscible solvents. In the case of the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand[5] the molecular extinction coefficient is 14,400 and is much to be preferred in sensitivity.

SUMMARY

A study has been made of 10 substituted 2,2'-diquinolines together with their physical constants involving maximum and minimum wavelengths of absorption and associated molecular extinction coefficients. An attempt has been made to interpret the results in relation to the π-electron distribution brought about by substitution of methyl or phenyl groups for hydrogen. The known proficiency of the phenyl groups as an electron donor as compared with the lesser tendency provided by the methyl alkyl group, previously clearly shown in the case of similar substitutions in 1,10-phenanthroline, has been found to apply in the case of 2,2'-diquinoline. The study of mono- and di-substitutions in the 3,4- and 4,4'-positions in 2,2'-diquinoline have been included. It is thought that a better understanding has been attained of the factors influencing structural modifications in the parent molecule which would be worthy of consideration in the case of future attempted developments. The most efficient diquinoline yet described, namely, 4,4'-diphenyl-2,2'-diquinoline (molecular extinction coefficient 9020, wavelength of maximum absorption 559 mμ), was obtained following the disclosed principles of structure.

RÉSUMÉ

Une étude a été effectuée sur dix 2-2' diquinoléines substituées, ainsi que sur leurs constantes physiques, y compris leur longueur d'onde d'absorption maximum et minimum, et leur coefficient d'extinction moléculaire. Les auteurs ont essayé d'interpréter les résultats par rapport à la distribution d'électrons π dans la molécule type et les variations observées après substitution de l'hydrogène par les radicaux méthyl et phényl. Lors de substitution, la propriété du groupement phényl de permettre à la molécule de céder plus facilement des électrons que le groupement méthyl, déjà connue pour la 1,10-phénanthroline se maniféste aussi pour la 2,2'-diquinoléine. On a également étudié les mono- et di-substitutions, dans les positions 3,4 et 4,4' de la 2,2'-diquinoléine. On estime que l'on arrive ainsi à une connaissance plus approfondie des facteurs influençant les modifications de structure de la molécule type pouvant servir aux futures recherches. La plus efficace des 2,2'-diquinoléines décrites, c'est-à-dire la 4,4'-diphényl-2,2'-diquinoléine, a été obtenue selon les principes de structure établis dans cette étude (coefficient moléculaire d'extinction: 9020; longueur d'onde d'absorption maximum: 559 mμ).

ZUSAMMENFASSUNG

Eine Untersuchung von zehn substituierten 2,2'-Dichinolinen und ihrer physikalischen Konstanten einschliesslich der Wellenlängen der Absorptionsmaxima und -minima und den damit verbundenen molaren Extinktionskoeffizienten wurde unternommen. Es wurde der Versuch unternommen die Ergebnisse in Bezug auf die Grösse der π-Elektronverteilung im Stammolekül und die durch die Substitution des Wasserstoffs mit Methyl- und Phenylgruppen hervorgerufenen Veränderungen der π-Elektronverteilung zu interpretieren. Es zeigte sich auch hier, wie schon früher bei ähnlichen Substitutionen beim 1,10-Phenanthrolin eindeutig gezeigt werden konnte, dass die Fähigkeit der Phenylgruppen als Elektrondonor zu spielen

verglichen mit der geringeren Tendenz der Methyl-Alkylgruppen auch im Falle des 2,2'-Dichinolin vorhanden ist. Die Untersuchung von Mono- und Di-substitutionen in den 3,4 und 4,4'-Stellungen des 2,2'-Dichinolins wurden ebenfalls einbegriffen. Wir denken, dass ein verbessertes Verständnis der die unternommenen Strukturänderungen im Stammolekül beeinflussenden Faktoren erreicht wurde, das wert ist bei zukünftig unternommenen Entwicklungen in Betracht gezogen zu werden. Das wirksamste, bisjetzt beschriebene Dichinolin, nämlich das 4,4'-Diphenyl-2,2'-Dichinolin (molarer Extinktionskoeffizient 9020, Wellenlänge des Absorptionsmaximum 559 mμ) wurde nach den entdeckten Strukturprinzipien bestimmt.

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COLORIMETRIC DETERMINATION OF ANIONIC DETERGENTS

by

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INTRODUCTION

Human and bovine albumin are capable of combining with various organic molecules[1]. During investigations on the interaction of anionic detergents and human albumin in the pH-sector where a precipitate is not formed, we observed the displacement of the dye in an albumin-bromcresol purple complex by the detergent. The amount of liberated dye was shown to be proportional to the amount of detergent added (within certain limits), and, as the protein complex showed a light absorption curve different from the free dye, the liberated dye could be determined colorimetrically.

EXPERIMENTAL

Human albumin and bromcresol purple form a blue complex over a fairly wide pH region. Our experiments were carried out at pH 5.1, using an acetate buffer of $\mu = 0.20$. Part of the absorption curves of albumin-bromcresol purple complex and free bromcresol purple (= BCP) are shown in Fig. 1. A very small amount of detergent added to the complex causes a marked increase of the extinction (Figs. 1c and 2), but on adding more detergent the dye is displaced from the complex and the extinction decreases proportionally with the detergent. The cause of the initial increase has not been proved, but may be a result of a denaturation of the protein by the detergent by which more groups capable of binding the dye may appear. The extinction was read in the Beckman DU spectrophotometer at 600 mμ, but the results with an ordinary photoelectric colorimeter were nearly as good.

Materials. Human albumin used showed only traces of globulin in electrophoresis. Analytical grade BCP (dibromo-*o*-cresolsulphophthalein, M.W. = 540) was used. Its solutions in buffer must not be used longer than 24 h, a 5 per cent. solution in ethanol is very convenient to prepare the necessary dilutions.

The method was checked with sodium dodecylsulphate, recrystallized 5 times from boiling absolute ethanol. Every solution was prepared in acetate buffer of pH 5.1, $\mu = 0.20$.

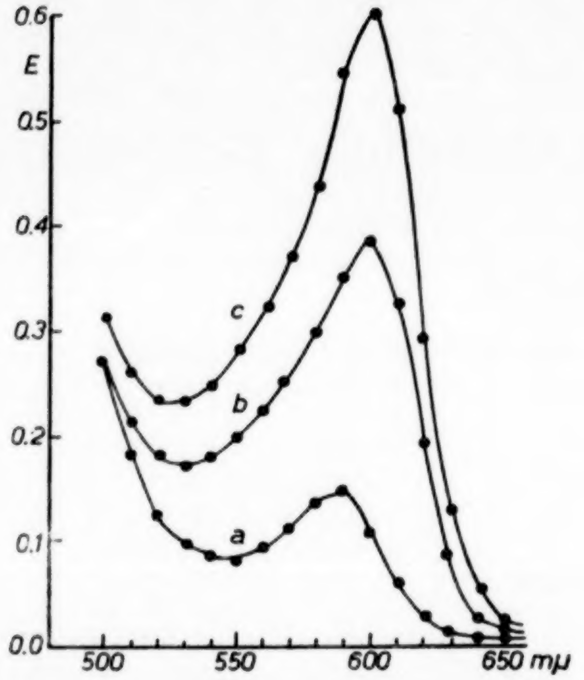

Fig. 1. Extinction curves of a) bromcresol purple; b) bromcresol purple-albumin complex; c) bromcresol purple-albumin complex with sodium dodecylsulphate, albumin/SDS mol. ratio = 1/5.

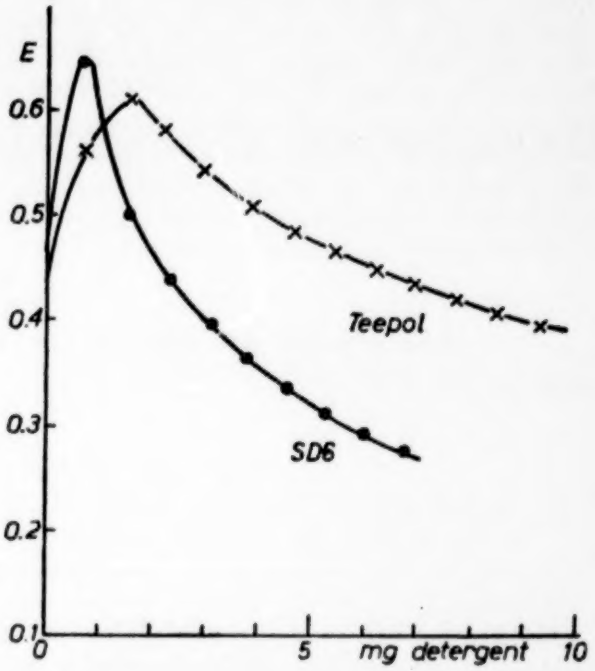

Fig. 2. Action of detergents on a bromcresol purple-albumin complex (see text) • = sodium dodecylsulphate = SDS; × = TEEPOL.
(for SDS: horizontal axis readings × 0.4)

METHOD

Calibration curve. To 4 ml 0.40 per cent. albumin solution in buffer is pipetted 2 ml 0.020 per cent. BCP in buffer, A ml (being 0.0-0.5-1.0 .... 5.0 ml) 0.050 per cent. sodium dodecylsulphate in buffer and 9-A ml buffer. Mix by inversion, let stand for 1 h and read in a photoelectric colorimeter at 600 mμ. The absolute weight of the detergent is plotted against the extinction. Calibration curves of several detergents are shown in Figs. 2 and 3.

Analysis of unknown solutions. To concentrated solutions a suitable volume of buffer may be added to adjust the pH to 5.1 and the detergent concentration to 10-50 mg per cent. Very

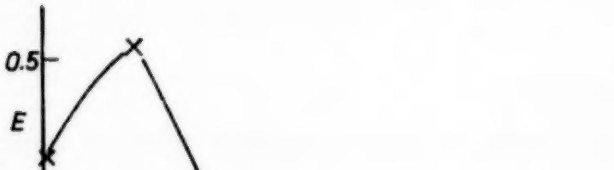

Fig. 3. Action of detergents on a bromcresol albumin complex. • = di-*iso*propylnaphthalene sulphonic acid = DINS; × = aerosol O.T.

dilute solutions should be concentrated first, and buffer added afterwards. Solid materials may be extracted with the buffer at room temperature. From the sample obtained in this way at least two different dilutions should be prepared, in order to avoid errors caused by the maximum in the calibration curve. Then proceed as mentioned under calibration curve.

RESULTS

The accuracy depends on the slope of the calibration curve. As is shown in Table I, the average accuracy is about 4%.

TABLE I

RECOVERIES*

amount in sol. mg	amount recovered mg	recovery per cent.
A. Sodium dodecylsulphate		
1.20	1.37	114
1.80	1.84	102
2.40	2.30	96
B. Teepol (about 20 per cent. sol. of alkyl sulphates C_{12}-C_{16})		
2.36	2.50	106
3.94	3.87	98
6.30	6.18	98
7.88	7.89	100
C. Aerosol OT (di-octyl sodium sulphosuccinate)		
0.64	0.66	102
1.28	1.25	97
1.82	1.98	103
D. Di-*iso*propylnaphthalene sulphonic acid		
0.40	0.36	90
0.80	0.79	99
1.20	1.22	101
1.60	1.58	99

* The technical assistance of Miss GINEKE J. BINKHORST is gratefully acknowledged.

Ions combining with one of the reagents of course interfere. Metal ions, and also those of the alkaline earths, should be removed. Neutral salts as NaCl do not interfere.

DISCUSSION

The present methods[2,3], are based on a complex formation between the detergent and a dye, which involves the extraction of the complex from the original solution, and the use of very unstable reagents. The method presented here is very rapid and simple, but its accuracy of about 4% is not so good as the claimed 2% of the rosaniline methods[2,3]. However as is shown above the protein complex method is not restricted to long chain alkyl sulphates, but may be used for many more anionic detergents.

References p. 150.

SUMMARY

Many types of anionic detergents can be determined colorimetrically by the action of the detergent on a protein-bromcresol purple complex. The amount of free dye liberated from the complex is proportional to the amount of detergent added between certain limits.

RÉSUMÉ

L'auteur décrit une méthode d'analyse colorimétrique pour le dosage des détergents anioniques. Le détergent agit sur un complexe protéine — bromocrésol-pourpre et il peut libérer ce colorant en quantité proportionnelle à sa propre concentration.

ZUSAMMENFASSUNG

Anionische Netzmittel sind imstande auf Albumin-Bromkresolpurpur-Komplexe einzuwirken und daraus den Farbstoff in einer Menge proportional zu ihrer eigenen Konzentration in Freiheit zu setzen. Da die Lichtabsorption des Farbstoffs und des Komplexes verschieden ist, ist es möglich die Menge Netzmittel quantitativ zu bestimmen.

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HETEROMETRIC MICROTITRATION OF ALUMINIUM WITH OXINE

by

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The determination of aluminium by precipitation with oxine is one of the most popular methods for the precipitation of aluminium with an organic reagent. Our aim was to study this reaction with the help of heterometry and to investigate the conditions necessary for a heterometric determination of aluminium. The heterometric method was developed in our laboratory during the last four years and many hundreds of chemical reactions were studied. The determinations of different metals by heterometric titration with oxine or vice versa were made. The results will be presented in special reports. Many experiments ware carried out with the aim of studying the course of the reaction of aluminium oxinate, the pH-dependency, the sensitivity, the analytical application and the accuracy. Only a small fraction of the titrations made are presented here. Most of the titrations were repeated at different time intervals. Generally a complete titration took between 5 and 15 minutes (this of course depends on the amount of points obtained) and the result was obtained from the curve plotted.

REMARKS

The sensitivity of a heterometric titration depends, among other factors, on the insolubility of the compound obtained. As the titrations of aluminium are made at room temperature and last only a few minutes, supersaturated solutions may be obtained. The first maximum optical density point indicates that the reaction is completed and serves for the determination of the analytical endpoint. The higher this value is for a definite concentration of a compound, the more sensitive generally should be the reaction studied. Unfortunately, in our case, as Figure 3 shows, the point of initial precipitation lies on the abscissa not far from the corresponding point of the first maximum optical density. Therefore, the lower limit of aluminium concentration which can be used for a heterometric titration is relatively high (0.001M).

References p. 155.

EXPERIMENTAL

All reagents used were either analytical reagents or chemically pure. Two different solutions of oxine were used; one was in 95% alcohol, the other was obtained by dilution of oxine with acetic acid. The description of the "Heterometer" (= photoelectric titrimeter) and the heterometric titration is given elsewhere[1-3]. All measurements with oxine were made with a yellow filter.

RESULTS

Composition of aluminium oxinate

The direct titration of a solution of aluminium with oxinate gives no evidence of the formation of intermediate compounds and only the final insoluble compound ($Al\ Ox_3$) is obtained. In the reverse titration, soluble as well as insoluble intermediates, which are marked by breaks in the heterometric curve obtained, can be clearly discerned. Fig. 1, curves 1 and 2, show the composition and the results of two such titrations. In both cases, on the abscissa, the point of the initial precipitation lies at the molar ratio 1 [Al] : 6 [oxine]. At this point the optical density rises very steeply. The maximum optical density lies at the ratio 1 [Al] : 3 [oxine]. On further addition of aluminium the optical density decreases. In curve 1 we may discern in addition, another break at the molar ratio 1 [Al] : 2 [oxine]. In both curves, the optical density decreases continuously with further addition of aluminium and the minimum optical density is reached almost exactly at the molar ratio 1 [Al] : 1 [oxine].

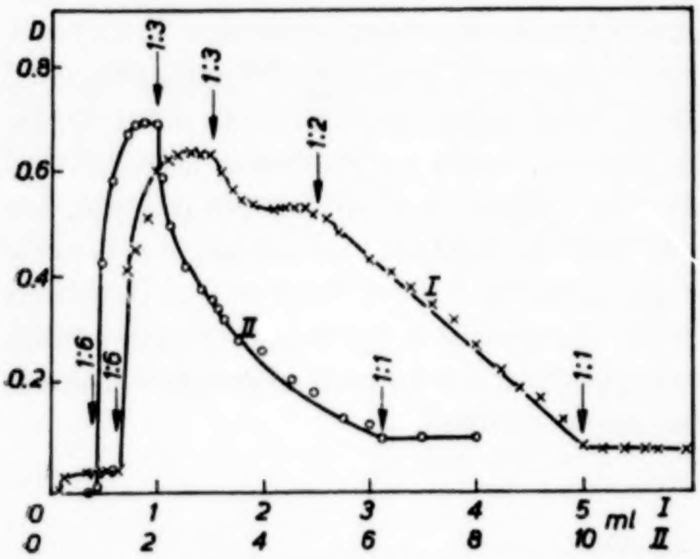

Fig. 1. 1. 5 ml 0.02M Oxine/0.1M acet. ac. + 3 ml Na-acetate + 32 ml H_2O + X ml 0.02M $AlCl_3$.
2. 2.5 ml 0.05M Oxine/50% alc. + 2 ml 1.0M Na-acetate + 3 ml 0.1M CH_3COOH + 32.5 ml H_2O + X ml 0.02M $AlCl_3$.

From these results we may deduce the existence of a soluble compound [Al Ox] and probably another one of the empirical composition $[Al\ Ox_6]_n$. In addition to the regular insoluble compound $[Al\ Ox_3]$, another insoluble intermediate compound of the composition $[Al\ Ox_2]$ may also exist.

pH titrations

Fig. 2 shows the composition and the results of two titrations, one measured heterometrically, the other a parallel pH titration.

The pH curve shows two inflexion points at pH = 6.5 and at pH = 10.5. At the lower point precipitation occurs. At the higher point the precipitate dissolves again.

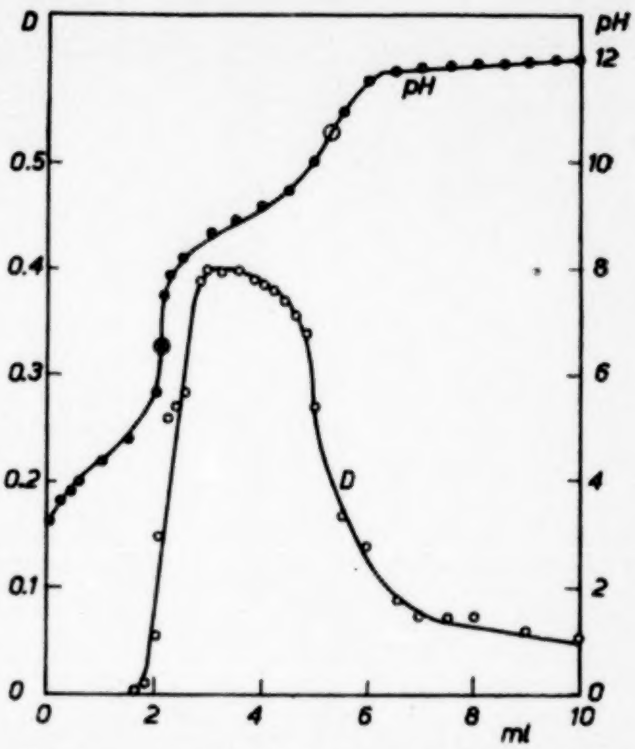

Fig. 2. Composition: 5 ml 0.01M $AlCl_3$ + 5 ml 0.01M Oxine + 2 ml 1.0M CH_3COOH + 3 ml 1.0M NH_4NO_3 + 25 ml H_2O + X ml 1.0M NaOH.

Determination of aluminium

Table I and Fig. 3 contain a selection of results of heterometric titrations of aluminium oxinate. The solutions contain 0.538 mg-1.345 mg of aluminium in a volume of either 20 ml or 40 ml. Both acetic acid and alcoholic solutions of oxinate were used. Although both series are not directly related, we see that generally, by titration with acetic oxine, lower maxima optical values are obtained (although the initial pH was even somewhat higher in the solutions titrated with alcoholic oxine). Generally the accuracy of the determination is not directly related to the magnitude of the maxima values. As to the influence of the different supplements, the following may be said: in the presence of sodium citrate even at the low concentration of 0.0025M, no precipitation occurs. The same concentration of sodium tartrate is without influence, but a higher concentration of tartrate (0.025M) causes perceptible errors (exp. 7). NH_4Cl present in a concentration of about 0.1M has hardly any influence on the results. Both solutions of oxine give results of the same accuracy between 0.5 γ and 0.0 γ per ml. One mg of aluminium (in 20 or 40 ml) may be determined heterometrically with an error of 0-2 per cent.

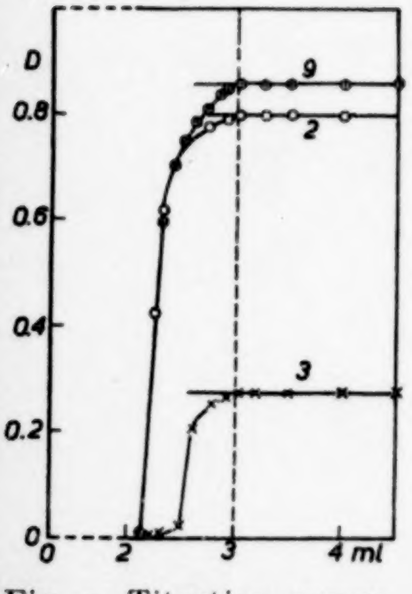

Fig. 3. Titration curves of aluminium chloride with oxine.

Method

1. The water solution contains ⩾ 0.5 mg of aluminium in 20 ml and is buffered with acetate to give a pH of 5.5-6. The titration is made with an alcoholic solution of 0.05M oxine.

2. 1-2 ml of 5M Na-acetate is added to about 20

References p. 155.

TABLE I

General composition:
a ml 0.01M $AlCl_3$ + b ml 1.0M Na acet. + C ml 0.1M CH_3COOH + d ml H_2O + X ml nM Oxine (in alcohol or CH_3COOH*).

Exper. number	Composition	Max.opt. density	Volume ml	content Al mg	content Al molarity	found Al mg	found Al x = ml	error mg	error γ/ml
1	5 ml $AlCl_3$ + 5 ml Na acet. + 30 ml H_2O + X ml 0.05M Oxine/acet.	0.319	40	1.345	0.00125	1.326	2.98	—0.019	—0.5
2	5 ml $AlCl_3$ + 2 ml Na acet. + 2 ml CH_3COOH + 31 ml H_2O + X ml 0.05M Ox/alc.	0.733	40	1.345	0.00125	1.326	2.98	—0.019	—0.5
3	5 ml $AlCl_3$ + 10 ml Na acet. + 25 ml H_2O + X ml 0.05M Ox/acet.	0.276	40	1.345	0.00125	1.322	2.96	0.022	—0.56
4	2 ml $AlCl_3$ + 3 ml Na acet. + 15 ml H_2O + X ml 0.02M Ox/acet.	0.244	20	0.538	0.001	0.529	2.95	0.009	—0.25
5	2 ml $AlCl_3$ + 6 ml Na acet. + 12 ml H_2O + X ml 0.02M Ox/acet.	0.308	20	0.538	0.001	0.538	3.0	0.0	0.0
6	5 ml $AlCl_3$ + 2 ml. Na acet + 3 ml CH_3COOH + 1 ml 0.1M Na_3Ci + X ml 0.05M Ox/alc.	0.0	40	1.345	0.001	0.0	0.0	—	—
7	5 ml $AlCl_3$ + 2 ml Na acet. + 2 ml CH_3COOH + 1 ml 0.1M Na_2Ta + X ml 0.05M Ox/alc.	0.831	40	1.345	0.00125	1.345	3.0	0.0	0.0
8	5 ml $AlCl_3$ + 2 ml Na acet. + 2 ml CH_3COOH + 2 ml 0.5M Na_2Ta + X ml 0.05M Ox/alc.	0.629	40	1.345	0.00125	1.457	3.25	+0.112	+2.8
9	5 ml $AlCl_3$ + 2 ml Na acet. + 2 ml CH_3COOH + 3 ml 1.0M NH_4Cl + 28 ml H_2O + X 0.05M Ox/alc.	0.854	40	1.345	0.00125	1.320	2.95	—0.025	—0.6
10	3 ml $AlCl_3$ + 2 ml Na acet. + 2 ml CH_3COOH + 33 ml H_2O + X ml 0.025M Ox/alc.	0.553	40	0.807	0.00077	0.828	3.7	+0.021	+0.5

* nM Oxine / 5nM CH_3COOH.

ml of water solution of an aluminium salt which contains ⩾ 0.5 mg aluminium. The titration is made with an 0.02-0.05M Oxine solution in acetic acid (CH_3COOH = 0.1-0.25M). The oxine is added drop by drop from a microburet (0.01 ml), while the solution is stirred vigorously. By drawing a line through the maxima values obtained, the endpoint (= first maximum optical density point) of the titration is obtained. A complete titration takes 5-15 minutes. Error = 0-2 per cent.

SUMMARY

The reaction of aluminium with oxine was studied by a new heterometric method. The composition of the intermediate compounds which are formed at room temperature are given. A method is presented for the determination of aluminium with oxine. ≥ 0.5 mg Al in 20 ml of solution may be determined in 5-15 minutes with an error between zero and 0.5 microgram per ml.

RÉSUMÉ

La réaction de l'aluminium avec l'oxine a été étudiée par une nouvelle méthode hétérométrique. La composition des dérivés intermédiaires, qui se forment à la température ordinaire, est donnée. Une méthode est présentée pour la détermination de l'aluminium par l'oxine. ≥ 0.5 mg Al peuvent être déterminés (dans 20 ml de solution) dans un temps de 5-15 minutes et avec une erreur de zéro à 0.5 microgrammes par ml.

ZUSAMMENFASSUNG

Die Reaktion von Aluminium mit Oxine wurde mit Hilfe der heterometrischen Methode studiert. Die bei gewöhnlicher Temperatur gebildeten intermediären Verbindungen wurden festgestellt. Eine Methode wird gebracht zur Bestimmung von Aluminium mit Oxin. ≥ 0.5 mg Aluminium kann in 20 ml Lösung innerhalb 5-15 Minuten mit einem Fehler von 0.0-0.5 µg per ml bestimmt werden.

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HETEROMETRIC MICRO-DETERMINATION OF MAGNESIUM WITH OXINE IN THE PRESENCE OF FOREIGN METALS

by

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INTRODUCTION

The aim of this work was to investigate the conditions necessary for a heterometric determination of magnesium, in the absence as well as in the presence of other salts or metals. Generally, the precipitation of magnesium is carried out at a higher temperature. As the following experiments show, the precipitation of magnesium oxinate at room temperature proceeds very slowly and therefore the constant readings of the galvanometer require more time than usual. A heterometric titration of magnesium lasted 30 to 40 minutes, which is about three times as long as is generally required for a heterometric titration at room temperature. In addition, the sensitivity of the magnesium determination is not very high: 0.4 to 1.0 mg of magnesium in 20 ml of an aqueous solution could be determined. After some experience the error was found to be nearly zero.

The following heterometric method presents the advantage of a *direct* determination of magnesium in the presence of an excess of foreign metals as aluminium, zinc, manganese, cadmium or calcium. In the latter cases, the determination was carried out in the presence of alkali citrate or tartrate. On the other hand the foreign metal itself can be determined directly at a lower pH (in the absence of a complex-binder) heterometrically by titration with the same oxine solution.

EXPERIMENTAL

All reagents used were either analytically or chemically pure. The same instrument and the same technique was used as in previous reports[1,2,3].

RESULTS AND DISCUSSION

Fig. 1 presents two parallel heterometric and pH titrations carried out under identical working conditions. It is interesting to note that the optical density curve (an orange filter was used in all titrations) shows an increase at a pH which

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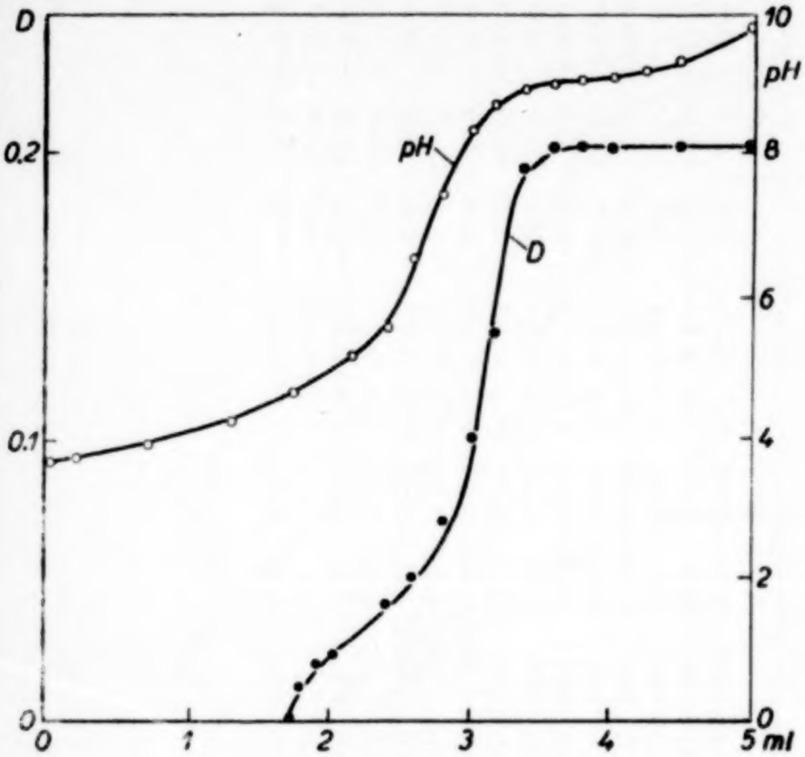

Fig. 1. Composition: 5 ml 0.01M $MgCl_2$ + 2 ml 1.0M CH_3COOH + 3 ml 1.0M NH_4NO_3 + 5 ml 0.02M 50% alc. oxine + 25 ml H_2O + X ml 1.0M NaOH.

is even lower than pH 7.0. Between pH 7 and 9 the density rises abruptly. A complete precipitation occurs at pH 9.0. Table I presents a selection of results which were obtained by titrations of solutions of different composition with oxine. The table gives the composition and the endpoint values obtained. In addition, Figs. 2 and 3 present (the experiment numbers are the same in the curves and in the table) the course of the titrations in the different cases. From the many titrations with magnesium which were carried out at different times, we found that the absolute values of the maxima densities obtained vary considerably. This probably must be explained by the exceedingly slow process of crystallisation. In no case did these fluctuations have any effect on the accuracy of the determination. The first eight experiments present titrations in the presence of magnesium only. Experiments 1, 2 and 4 show titrations with different amounts of magnesium. It can be seen that the accuracy of the determination does not depend on the absolute amount of magnesium present. On the other hand,

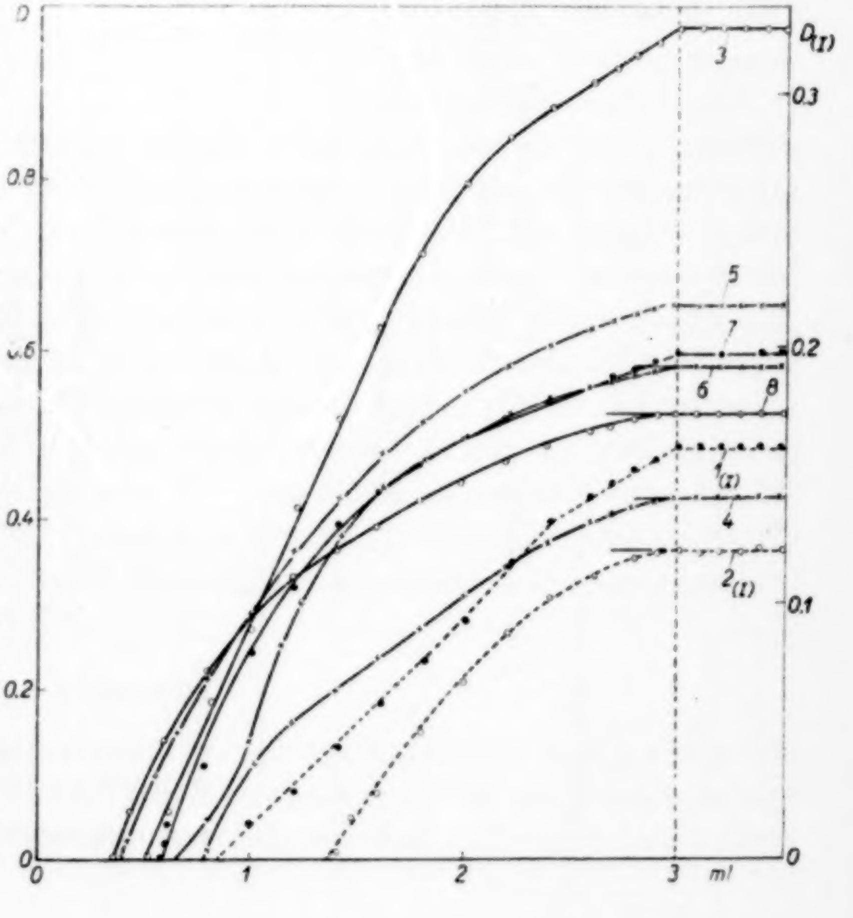

Fig. 2. Composition: 5 ml aM $MgCl_2$ + 5 ml 4M NH_3 + 1 ml 1.0M NH_4NO_3 + 9 ml supplementary X ml bM 50% alc. oxine.

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TABLE I

General composition:

5 ml aM $MgCl_2$ + 5 ml $4M$ NH_3 + 1 ml $1.0M$ NH_4NO_3 + 9 ml supplementary + X ml bM Oxine, 50% alc.
Vol: 20 ml; Filter: orange; Temp: 15 — 18.5°

Exp. No.	Supplementary	$MgCl_2$ Molarity	Mg		Used Oxine		Initial precip.	Max. density	Error		
			mg	%	ml	molar	at ml	value	%	γ	γ/ml
1	9 ml H_2O	0.003	0.3648	100	3.0	0.01	0.8	0.16	0.0	0.0	0.0
2	9 ,, ,,	0.003	0.3648	100	2.9	0.01*	1.4	0.12	—3.3	12.0	—0.6
3	9 ,, ,,	0.006	0.7296	100	3.0	0.01	0.5	0.33	0.0	0.0	0.0
4	9 ,, ,,	0.01	1.216	100	2.98	0.03	1.0	0.42	—0.7	8.5	—0.4
5	7 ,, ,, +2 ml 1.0M Na_3-citrate	0.01	1.216	100	2.95	0.03	0.4	0.65	—1.7	20.6	—1.0
6	5 ,, ,, +4 ,, 1.0 ,, ,, ,,	0.01	1.216	100	2.98	0.03	1.0	0.57	—0.7	8.5	—0.4
7	7 ,, ,, +2 ,, 1.0 ,, K_2-tartrate	0.01	1.216	100	3.0	0.03	0.6	0.6	0.0	0.0	0.0
8	5 ,, ,, +4 ,, 1.0 ,, ,, ,,	0.01	1.216	100	2.95	0.03	0.4	0.52	—1.7	20.6	—1.0
9	— 4 ,, 1.0 ,, Na_3-citrate +5 ml 0.1M $AlCl_3$	0.01	1.216	8.1	3.00	0.03	1.0	0.46	0.0	0.0	0.0
10	— 4 ,, 1.0 ,, K_2-tartrate +5 ,, 0.1 ,, ,,	0.01	1.216	8.1	3.05	0.03	0.8	0.39	+1.7	20.6	+1.0
11	3 ml H_2O +4 ,, 1.0 ,, Na_3-citrate +2 ,, 0.1 ,, ,,	0.01	1.216	18.2	3.0	0.03	0.7	0.78	0.0	0.0	0.0
12	— 4 ,, 1.0 ,, ,, ,, +5 ,, 0.1 ,, $Zn(NO_3)_2$	0.01	1.216	3.7	2.95	0.03	0.2	0.58	—1.7	20.6	—1.0
13	3 ml H_2O +4 ,, 1.0 ,, ,, ,, +2 ,, 0.1 ,, $MnCl_2$	0.01	1.216	11.0	2.9	0.03	1.60	0.89	—3.3	41.0	—2.0
14	3 ,, ,, +4 ,, 1.0 ,, ,, ,, +2 ,, 0.1 ,, $Cd(NO_3)_2$	0.01	1.216	5.0	3.0	0.03	1.40	0.39	0.0	0.0	0.0
15	3 ,, ,, +4 ,, 1.0 ,, ,, ,, +2 ,, 0.1 ,, $Ca(NO_3)_2$	0.01	1.216	13.0	2.98	0.03	1.60	0.66	—0.7	8.5	—0.4

* In 0.05 acetic acid.

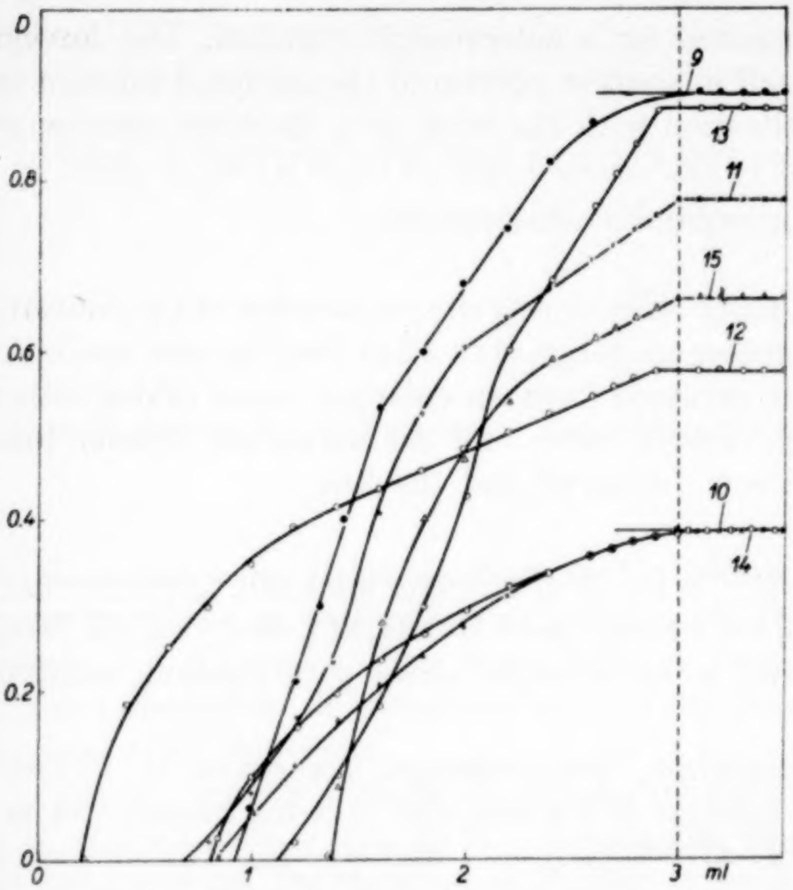

Fig. 3. Composition: 5 ml aM $MgCl_2$ + 5 ml $4M$ NH_3 + 1 ml $1.0M$ NH_4NO_3 + 9 ml supplementary + X ml bM 50% alc. Oxine.

the *sensitivity* (= minimum amount of metal which is required for a reliable titration) must be related to the height of the maximum value of a given amount of analysed metal. For comparison, titration number 2 was carried out with oxine in acetic acid solution. The titration proceeded slowly and the endpoint was uncertain.

The experiments 5-8 were carried out in the presence of a metal complex binder. As can be seen the accuracy is not affected by the presence of the supplements. As experiments 9-15 show, the points of the initial precipitation and the maxima values obtained, both depend on the character of the foreign metal and on its concentration. The various foreign metals were all tested in concentrations higher than those given in the table, but generally no definite maximum point near the calculated endpoint of the titration was obtained, (the density values rose indefinitely). Experiments 9-15 show that magnesium could be determined *directly* in solutions containing large excesses of aluminium, zinc, manganese, cadmium or calcium if sufficient sodium citrate (or tartrate) was added to the solution. Aluminium and zinc could be present in even higher molar concentration than the other metals. In most of these cases the error in the determination of magnesium was found to be almost zero. The possibility of masking considerable amounts of foreign metals in the presence of citrate or tartrate may be partly explained by the increased stability of the complexes concerned at room temperature.

CONCLUSION

With some experience in the heterometric determination of magnesium, the latter may be determined with almost theoretical results. The only disadvantage of the method is that the precipitation occurs slowly and a titration takes three times as long as is generally required for a heterometric titration. The foreign metal may be determined by itself in another portion of the analysed solution at a lower pH by a heterometric titration with the same 50% alcoholic solution of oxine (see special reports).

DETERMINATION OF MAGNESIUM

Technique

The solution is stirred continuously (even during the preparation of the mixture) and the readings of the galvanometer are taken only when they become constant. The endpoint of the titration is obtained from an enlarged curve taking either the point of intersection of the density curve and the maximum density line, or the first contact point between the curve and the line.

Method

In the absence of foreign metals: To 15 ml of a magnesium salt solution which contains $\gtrsim$ 1 mg of magnesium, are added: 1 ml 1*M* NH_4NO_3 and 5 ml 4*M* NH_3. The solution is then titrated with a 0.01-0.003*M* molar 50% alcoholic solution of oxine.

In the presence of excess aluminium, zinc, cadmium, manganese or calcium: To 15 ml of a magnesium salt solution which contains $\gtrsim$ 1 mg magnesium, are added: 1 g Na_3-citrate + 1 ml 1.0*M* NH_4NO_3 + 5 ml 5*M* NH_3. The solution is then titrated with 0.01-0.003*M* 50% alcoholic solution of oxine.

In both cases, after some experience, theoretical results for magnesium are mostly obtained. If the approximate amount of magnesium is unknown, it is advisable to make a rough titration and only then to make the final titration.

SUMMARY

A heterometric method was presented for the direct determination of magnesium with oxine in the presence of excesses of aluminium, zinc, cadmium, manganese or calcium. $\gtrsim$ 1 mg of magnesium in 20 ml solution could be determined with an error which generally equalled zero.

RÉSUMÉ

Une méthode hétérométrique est présentée pour la détermination directe du magnésium par l'oxine, en présence d'un excès d'aluminium, zinc, cadmium, manganèse et calcium. $\gtrsim$ 1 mg de magnésium (dans 20 ml de solution) peuvent être determinés avec une erreur généralement presque nulle.

ZUSAMMENFASSUNG

Eine heterometrische Methode wird gebracht zur direkten Bestimmung von Magnesium mit Oxin in Gegenwart von Überschüssen von Aluminium, Zink, Cadmium, Mangan oder Calcium. $\gtrsim$ 1 mg Magnesium konnte in 20 ml Lösung bestimmt werden. Der Fehler war in allgemeinen nahezu Null.

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SUR L'INTENSITÉ DU COURANT PENDANT UN TITRAGE „DEAD STOP"

par

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Dans une série d'articles, GAUGUIN[1] a déduit les phénomènes qui peuvent se présenter dans les méthodes basées sur la polarisation. Le raisonnement mathématique a été conçu d'une façon très générale, de sorte que le cas simultané d'une polarisation de concentration et d'une polarisation d'activation a été pris comme point de départ.

Lors de l'emploi d'électrodes de platine surtout, quand il s'agit de systèmes irréversibles dans le sens de la polarographie, le potentiel de l'électrode s'établit si lentement que ces systèmes ne se prêtent pas à la vérification numérique de la théorie.

Dans le présent article nous déduirons par une autre méthode la courbe des titrages „dead-stop" pour les cas réversibles, en nous basant sur l'équation du polarogramme d'un système Redox réversible dont les deux composantes sont dans la solution.

Au cas d'un système Redox réversible $OX + z_i\ e = R$, le potentiel d'une électrode traversée par le courant peut être représenté, quand il ne s'agit que d'une polarisation de concentration, par l'équation[2]

$$\varepsilon = \varepsilon_0 + \frac{R \cdot T}{z_i \cdot F_y} \ln \frac{K_{ox}{}^*[OX] - i}{K_R{}^*[R] + i} \sqrt{\frac{D_R}{D_{ox}}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

dans laquelle *i* possède une valeur positive quand le courant dans la solution se rend à l'électrode.

Si nous plaçons dans la solution deux électrodes entre lesquelles une différence de potentiel constante est appliquée, le même courant les traversera naturellement toutes les deux. Dans la formule (1) le signe devant le *i* devra cependant changer de sorte que nous aurons:

$$\pi_{an} = \varepsilon_0 + \frac{R \cdot T}{z_i \cdot F_y} \ln \frac{K_{ox}{}^*[OX] + i}{K_R{}^*[R] - i} \sqrt{\frac{D_R}{D_{ox}}} \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$\pi_C = \varepsilon_o + \frac{R{\cdot}T}{z_i \cdot F_y} \ln \frac{K_{ox}{*}[\mathrm{OX}] - i}{K_R{*}[\mathrm{R}] + i} \sqrt{\frac{D_R}{D_{ox}}} \quad \ldots\ldots\ldots\ldots \quad (3)$$

On peut donc écrire pour la différence de potentiel appliquée $\triangle$:

$$\triangle = \pi_{an} - \pi_C = \frac{R{\cdot}T}{z_i \cdot F_y} \ln \frac{\{K_{ox}{*}[\mathrm{OX}] + i\}\{K_R{*}[\mathrm{R}] + i\}}{\{K_{ox}{*}[\mathrm{OX}] - i\}\{K_R{*}[\mathrm{R}] - i\}} \quad \ldots\ldots\ldots \quad (4)$$

comme différence des équations (2) et (3).

Pendant un titrage, $*[\mathrm{OX}]+*[\mathrm{R}]$ reste constant, de sorte que nous pouvons écrire

$$*[\mathrm{OX}] + *[\mathrm{R}] = *[C] \quad \ldots\ldots\ldots\ldots \quad (5)$$

De plus $*[\mathrm{OX}] = x \cdot *[C]$ .... (6)

et $*[\mathrm{R}] = (1-x) \cdot *[C]$ .... (7)

Nous avons pour but de trouver i en fonction de x.

Supposons pour abréger que

$$K_{ox} \cdot x \cdot *[C] = a \quad \ldots\ldots\ldots\ldots \quad (8)$$

et $$K_R \cdot (1-x) \cdot *[C] = b \quad \ldots\ldots\ldots\ldots \quad (9)$$

En ce cas l'équation (4) sera:

$$\triangle = \frac{R{\cdot}T}{z_i \cdot F_y} \ln \frac{(a+i)\ (b+i)}{(a-i)\ (b-i)} \text{ ou}$$

$$e^{\triangle / \frac{R\cdot T}{z_i \cdot F_y}} = \triangle' = \frac{(a+i)\ (b+i)}{(a-i)\ (b-i)} \quad \ldots\ldots\ldots\ldots \quad (10)$$

Dans l'équation (10) nous pouvons résoudre i en fonction de a et b, donc (voir 8 et 9) en fonction de x.

Une simplification peut être faite si nous mettons

$$K_R = K_{OX} = K \quad \ldots\ldots\ldots\ldots \quad (11)$$

Etant donné que K est proportionnel à $D^{\frac{1}{2}}$, il s'ensuit que, pour des ions qui ne diffèrent l'un de l'autre que dans la valeur de la charge, la différence entre K_{OX} et K_R ne représentera qu'un petit pourcentage.

En substituant (8), (9) et (11) dans l'équation (10) nous avons trouvé

$$i = \frac{K.*[C]}{2} \cdot \frac{\triangle' + 1}{\triangle' - 1} \left[1 - \sqrt{\left\{ 1 - 4\left(\frac{\triangle' - 1}{\triangle' + 1}\right)^2 \cdot x \cdot (1-x) \right\}} \right] \quad \ldots\ldots\ldots \quad (12)$$

Cette équation représente la branche inférieure d'une hyperbole qui est symétrique par rapport à $x = \frac{1}{2}$.

Le courant maximum est:

$$i_m = \frac{K\cdot{}^*[C]}{2}\cdot\frac{\triangle'+1}{\triangle'-1}\left[1-\sqrt{\left\{1-\left(\frac{\triangle'-1}{\triangle'+1}\right)^2\right\}}\right]$$

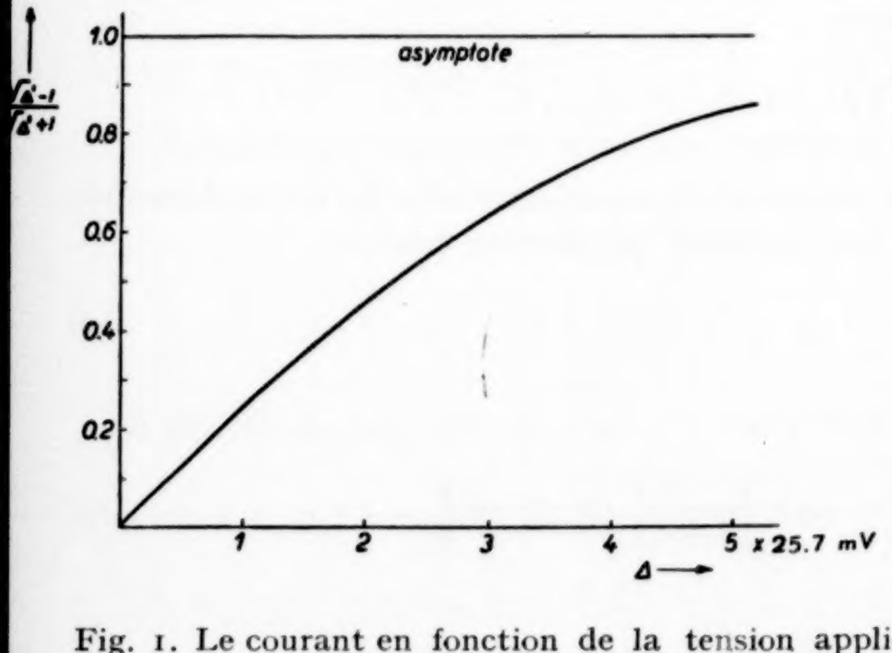
ou, après simplification:

$$i_m = \frac{K\cdot{}^*[C]}{2}\cdot\frac{\sqrt{\triangle'}-1}{\sqrt{\triangle'}+1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

Le courant dépend d'une manière complexe de la différence de potentiel (Fig. 1, Tableau I).

TABLEAU I

$\triangle$	0	0.1	0.2	0.4	1	2	3	4	∿	×25.7 mV
$\triangle'$	1	1.105	1.221	1.492	2.718	7.389	20.08	54.6	∿	
$\sqrt{\triangle'}$	1	1.051	1.105	1.221	1.649	2.718	4.480	7.389	∿	
$\frac{\sqrt{\triangle'}-1}{\sqrt{\triangle'}+1}$	0	0.0249	0.0499	0.0995	0.245	0.462	0.635	0.762	1	



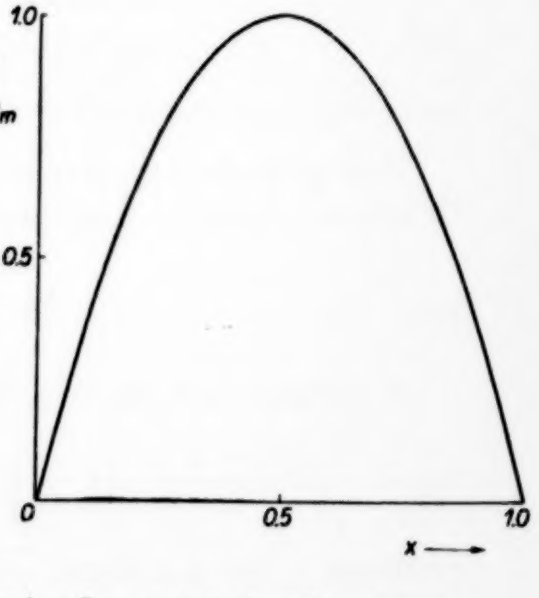


Fig. 1. Le courant en fonction de la tension appliquée. Le courant est proportionnel à l'ordonnée.

Fig. 2. Courbe de variation du courant relatif j_m en fonction de la fraction ayant réagi.

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TABLEAU II

x	j_m
0	0
0.05	0.185
0.10	0.360
0.15	0.510
0.20	0.640
0.25	0.750
0.30	0.840
0.40	0.960
0.50	1
0.60	0.960
0.70	0.840
0.75	0.750
0.80	0.640
0.85	0.510
0.90	0.360
0.95	0.185
0	0

Pour de petites différences de potentiel, i_m est proportionnel à celles-ci, ce qui résulte en développant:

$$\frac{\sqrt{\triangle'} - 1}{\sqrt{\triangle'} + 1} = \frac{e^{\triangle / \frac{R \cdot T}{z_i \cdot F_v}} - 1}{e^{\triangle / \frac{R \cdot T}{z_i \cdot F_v}} + 1} = \frac{e^{p} - 1}{e^{p} + 1}$$

dans une série:

$$\frac{e^{p} - 1}{e^{p} + 1} = \tfrac{1}{2}\, p - \tfrac{1}{4} \cdot \tfrac{1}{3!} \cdot p^3 + \ldots\ldots\ldots$$

Pour pouvoir comparer plus facilement les expériences avec la courbe théorique, il est avantageux d'adopter une intensité de courant relative

$$j_m = \frac{i}{i_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

Il résulte alors de (12), (13) et (14):

$$j_m = \frac{\triangle' + 1}{(\sqrt{\triangle'} - 1)^2} \cdot \left[1 - \sqrt{\left\{1 - 4\left(\frac{\triangle' - 1}{\triangle' + 1}\right)^2 \cdot x \cdot (1 - x)\right\}}\right] \quad \ldots\ldots\ldots \quad (15)$$

$$\text{Pour } \left.\begin{array}{l} \triangle = 5 \text{ mVolts} \\ t = 25^\circ \text{C} \\ z_i = 1 \end{array}\right\} \text{ ou } \triangle' = 1.215$$

il résulte le Tableau II pour j_m et x (Fig. 2).

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Pour la valeur de $\frac{\mathrm{d}j_m}{\mathrm{d}x}$ au début et à la fin du titrage nous pouvons déduire

$$\left[\frac{\mathrm{d}j_m}{\mathrm{d}x}\right]_{\substack{x=0\\x=1}} = \pm 2\,\frac{\sqrt{\triangle'}+1}{\triangle'+1}$$

Une petite modification se présente quand nous avons aussi à faire avec un système Redox réversible après le point d'équivalence.

Supposons que nous ayons dans la burette un agent oxydant et qu'avec celui-ci un agent réducteur ait été exactement converti jusqu'au point d'équivalence. Si nous ajoutons un excès du réactif, la concentration du liquide de titrage réduit restera donc constante $^*[C_{\mathrm{R}}]$. Nous exprimons l'excès du réactif dans cette concentration: $^*[C_{\mathrm{OX}}] = y^*.[C_{\mathrm{R}}]$.

Il y a donc au total

$$^*[C_{\mathrm{OX}}] + {}^*[C_{\mathrm{R}}] = (y+1)^*[C_{\mathrm{R}}]$$

La fraction x (voir équation 6) est donc en ce cas: $\frac{y}{y+1}$

L'équation (12) se change maintenant en:

$$i = (y+1)\,\frac{K\cdot{}^*[C_{\mathrm{R}}]}{2}\cdot\frac{\triangle'+1}{\triangle'-1}\left[1-\sqrt{\left\{1-4\left(\frac{\triangle'-1}{\triangle'+1}\right)^2\cdot\frac{y}{y+1)^2}\right\}}\right] \quad \ldots\ldots \quad (16)$$

Si nous établissons cette expression par rapport à la valeur i_1, qui représente l'intensité du courant quand $y = 1$, nous trouvons:

$$j_1 = \frac{i}{i_1} = \frac{\triangle'+1}{(\sqrt{\triangle'}-1)^2}\cdot\frac{y+1}{2}\left[1-\sqrt{\left\{1-4\left(\frac{\triangle'-1}{\triangle'+1}\right)^2\cdot\frac{y}{(y+1)^2}\right\}}\right] \quad \ldots \quad (17)$$

L'équation (17) représente aussi une hyperbole. Pour l'abréger nous écrivons:

$$\tfrac{1}{2}\cdot\frac{\triangle'+1}{(\sqrt{\triangle'}-1)^2} = A \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

$$\left(\frac{\triangle'-1}{\triangle'+1}\right)^2 = B \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

Il résulte de (17), (18) et (19).

$$j_1 = \mathrm{A}\cdot(y+1)\left[1-\sqrt{\left\{1-4\,B\,\frac{y}{(y+1)^2}\right\}}\right] \text{ ou}$$

$$j_1^2 - 2\,A\cdot j_1\cdot y - 2\,A\cdot j_1 + 4\,A^2\cdot B\cdot y = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

Nous trouvons le centre de l'hyperbole en différentiant partiellement (20) selon j_1 et selon y:

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$$2\,j_1 - 2\,A\cdot y - 2\,A = 0 \quad \ldots\ldots \quad (21)$$

$$-2\,A\cdot j_1 + 4\,A^2\cdot B = 0 \quad \ldots\ldots \quad (22)$$

(21) et (22) combinées donnent la position du centre.

$$[j_1]_C = 2\,A\cdot B$$
$$y_C = 2\,B - 1$$

Il résulte de (20) que les directions asymptotiques répondent à l'équation

$$j_1^2 - 2\,A\cdot j_1\cdot y = 0, \text{ c.à.d. } j_1 = 0$$
$$\text{et} \quad j_1 = 2\,A\cdot y$$

Les équations des asymptotes deviennent

$$j_1 = 2\,A\cdot B \qquad \text{(horizontale)}$$
$$\text{et} \quad j_1 - 2\,A\cdot B = 2\,A\cdot(y - 2\,B + 1)$$
$$\text{ou} \quad j_1 - 2\,A\cdot y + 2\,A\cdot B - 2\,A = 0$$

La première asymptote (c'est celle-ci qui nous intéresse) est parallèle à l'abscisse à une hauteur

$$j_1 = \frac{(\sqrt{\triangle'} + 1)^2}{\triangle' + 1}$$

Pour les mêmes valeurs de $\triangle$, t et z_i il en résulte maintenant le Tableau III et Fig. 3 pour j_1 en fonction de y.

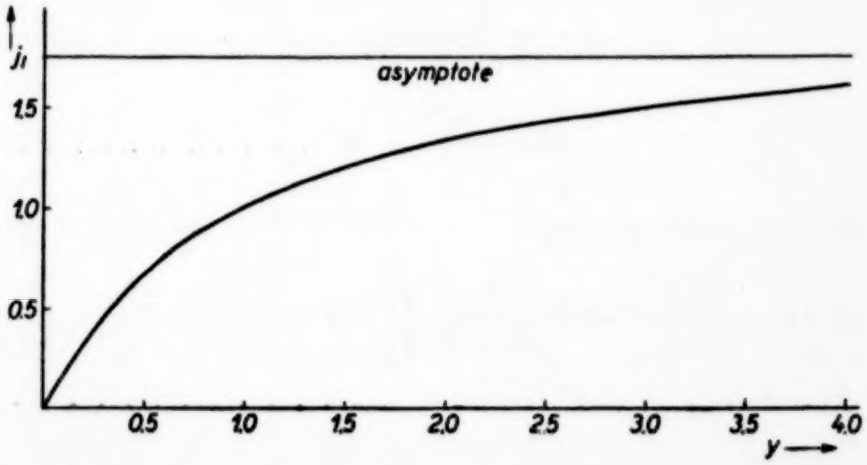

Fig. 3. Courbe de variation du courant relatif j_1 en fonction de l'excès relatif y du réactif.

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TABLEAU III

y	j_1
0.1	0.182
0.2	0.333
0.3	0.463
0.4	0.570
0.6	0.751
0.8	0.887
1	1.000
1.5	1.197
2	1.329
2.5	1.418
3	1.492
4	1.601
5	1.666
10	1.807
$\sim$	1.994

Pour les petits voltages, j_m et j_1 en sont indépendants. Il sera démontré dans un article suivant que les résultats des déductions mathématiques concordent avec les mesures.

RÉSUMÉ

On a établi par déduction une formule pour l'intensité du courant en fonction de la quantité de réactif pendant un titrage ,,dead-stop'' dans le cas d'un système-Redox réversible.

SUMMARY

A formula has been derived for the intensity as a function of the reagent during a "dead-stop" titration, when a reversible redox system is present.

ZUSAMMENFASSUNG

Man hat eine Formel abgeleitet für die Stromintensität als Funktion des zugesetzten Reagenzes während einer ,,dead-stop'' Titration, im Falle eines reversiblen Redox-Systems.

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QUINQUEVALENT TUNGSTEN AS A REDUCING AGENT IN POTENTIOMETRIC TITRATIONS

by

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In studying the applicability of quinquevalent molybdenum as a volumetric reagent, the compound was found suitable for the determination of a number of higher-valent ions from which may be mentioned dichromate, vanadate, iodate, ceric and ferric ions[1]. The object of the present investigation is to find out whether quinquevalent tungsten can be used for similar purposes. Measurements of the formal redox potentials of the system W^{+6}/W^{+5} showed that they amount to 0.247 and 0.108 volt in 10.5 and 8*N* hydrochloric acid respectively as compared with 0.470 volt for the system Mo^{+6}/Mo^{+5} in 8*N* HCl[2] indicating that quinquevalent tungsten is more reducing than the corresponding molybdenum compound.

EXPERIMENTAL

Preparation of quinquevalent tungsten solutions

Quinquevalent tungsten solutions were obtained by the electrolytic reduction of sodium tungstate in 10*N* hydrochloric acid. The process of reduction was performed in a cell having a capacity of 500 ml with a blank platinum spiral anode and a platinised perforated platinum cathode of an apparent area = 60 sq.cm., separated from each other by a sintered glass diaphragm. The current density amounted to 0.02 amp per cm^2 of apparent area. Under these conditions reduction proceeds only to the quinquevalent state[3]. Throughout the process, the acidity was kept above 8*N* hydrochloric acid so as to avoid the precipitation of tungstic acid.

The titration device

The titration vessel consisted of a well steamed Pyrex glass beaker fitted with a rubber stopper that had been previously boiled in dilute hydrochloric acid. The stopper had holes for the tip of the burette, the stirrer with its mercury seal, the indicator electrode consisting of a platinum sheet 2 cm^2 in area, the salt bridge filled with saturated potassium chloride solution and connecting the saturated calomel electrode and for the entrance and exit of CO_2.

The quinquevalent tungsten solutions were delivered from a Zintl Storage apparatus and the titrations performed in a current of pure CO_2. All the reagents were freed from dissolved oxygen by CO_2.

RESULTS AND DISCUSSION

Standardisation of quinquevalent tungsten solutions

Quinquevalent tungsten was determined by potentiometrically titrating appropriate volumes with standard potassium dichromate solution. In preparing the latter as primary standard, the procedure recommended by FURNESS[4] was adopted. As it was desirable in these titrations to maintain the hydrochloric acid concentration at $2N$[5] within which range tungsten trioxide is liable to separate out, sufficient phosphoric acid was added to retain it in solution in the form of soluble heteropoly complex.

As a measure for the accuracy of the reaction one can calculate with the help of the redox potentials of the systems concerned and the formal redox potentials as obtained from the titration curves, K the equilibrium constant and α the degree of completion for the respective reactions, *i.e.* the fraction of oxidant or reductant that fails to react at the equivalence point. For this purpose the relations:

$$\log K = z\,(E_{f1}\text{-}E_{f2})/0.059 \quad \text{and} \quad \alpha = K^{(1/n_1 + n_2)}$$

can be used in which n_1 and n_2 represent the respective valency changes for both pairs of ions, E_{f1} and E_{f2} the formal potentials of the first and the second systems respectively and z the number of faradays necessary to complete the reaction.

SMITH AND RICHTER[6], obtained from potentiometric titrations with dichromate ions in hydrochloric acid of concentrations varying between 1 to $4N$ formal potential values for the system Cr^{+6}/Cr^{+3} which do not seem to vary appreciably with acid concentration. Taking 1.11 and 0.177 volt to represent E_f for the Cr^{+6}/Cr^{+3} and W^{+6}/W^{+5} systems in $2N$ HCl and $2N$ H_3PO_4 (see below) K and α amount to $5.4 \cdot 10^{-48}$ and $1.5 \cdot 10^{-12}$ respectively. From the titration curve (Fig. 1), E_f amounts under the same conditions to 0.7 volt, accordingly K and α amount to $2.6 \cdot 10^{-27}$ and $2.2 \cdot 10^{-7}$ respectively.

Trials were further made to oxidise quinquevalent tungsten solutions in $8N$ HCl with dichromate. EPPLEY AND VOSBURGH[5] titrated dichromate solutions with ferrous iron at concentrations of HCl as high as $6N$ at which acidity, their results did not deviate appreciably from the theoretical values. Trials to perform the titrations of quinquevalent tungsten in $8N$ HCl led to results which agreed closely with those obtained at lower acidities in presence of phosphoric acid. The E_f value of the Cr^{+6}/Cr^{+3} couple at this acidity as obtained from the

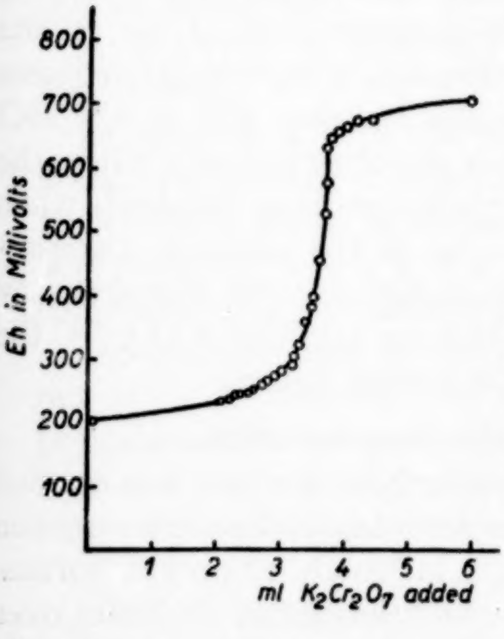

Fig. 1. Standardisation of 0.0170 N W^{+5} with 0.1130 N $K_2Cr_2O_7$.

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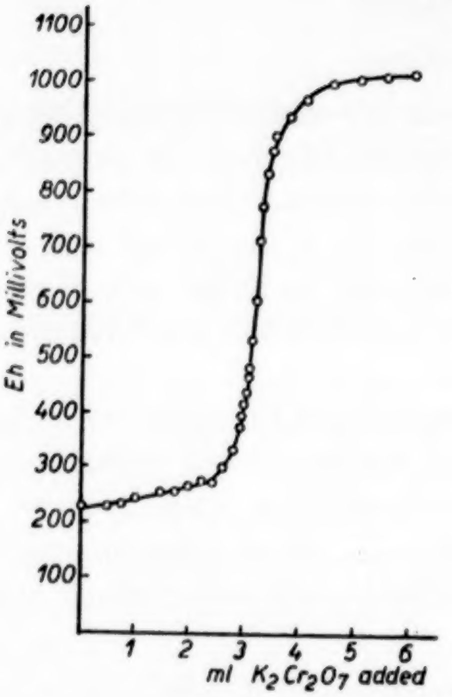

Fig. 2. Titration of 0.0109 N W^{+5} with 0.100 N $K_2Cr_2O_7$.

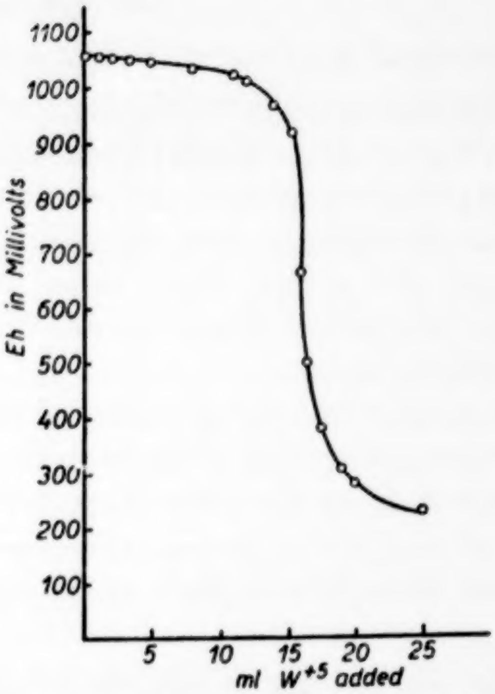

Fig. 3. Titration of 0.010 N $K_2Cr_2O_7$ with 0.0123 N W^{+5}.

titration curve (Fig. 2) and amounting to 1.05 volt appears thus to permit the titrations to be performed without the interference of hydrochloric acid ($E_{0\frac{1}{2}}Cl_2/Cl^-$ = 1.36 volt). Using 0.108 volt to represent E_f for the W^{+6}/W^{+5} system in 8N HCl, K and a amount under these conditions to $1.3 \cdot 10^{-48}$ and $1.1 \cdot 10^{-12}$ respectively.

In Table Ia are recorded some of the results obtained by titrating different amounts of quinquevalent tungsten with potassium dichromate under varying conditions of temperature and acidity. Table Ib contains some of the results obtained under similar conditions for the reverse titration, a representative curve of which in 8N HCl is shown in Fig. 3. The results indicate that in 8N HCl considerable deviations from the theoretical values are observed only when the titration is performed at 50° C. At 25° C reliable results are only obtained when the total amount of W^{+5} titrated exceeds ∿ 20 mg in the solution. Determination of dichromate with W^{+5} solutions can be performed with fair accuracy if the titration is performed in 8N HCl at 25° C. At lower acidities or at 50° C the results show considerable deviations from the theoretical values.

Stability and speed of oxidation of quinquevalent tungsten solutions

The stability of the W^{+5} solution towards atmospheric oxygen was studied under a variety of conditions. For this purpose samples of quinquevalent tungsten in 10, 8, 6, 4, 2 and 1N HCl solutions were kept in loosely stoppered bottles. Samples were withdrawn by means of a pipette at intervals of 12 hours over 3 days and titrated using a standard potassium dichromate solution. From the results obtained it was found that:

TABLE Ia

	mg W^{+5} present	mg W^{+5} found	Error %
W^{+5} in 8*N* HCl at 25° C	59.87	59.77	0.17
,, ,, ,, ,, ,, ,,	39.91	39.850	0.15
,, ,, ,, ,, ,, ,,	19.96	20.04	0.4
,, ,, ,, ,, ,, 50° C	39.91	37.36	6.39
,, ,, 2*N* HCl 2*N*H_3PO_4 at 25° C	77.89	77.88	0.01
,, ,, ,, ,, ,, ,, ,, ,,	17.71	17.63	0.47

TABLE Ib

	mg $Cr_2O_7^{-2}$ present	mg $Cr_2O_7^{-2}$ found	Error %
$Cr_2O_7^{-2}$ in 3.6*N* HCl at 25° C	32.80	32.09	2.15
,, ,, 5*N* ,, ,, ,,	32.80	32.51	0.87
,, ,, 8*N* ,, ,, ,,	32.80	32.74	0.18
,, ,, ,, ,, ,, ,,	16.40	16.44	0.25
,, ,, ,, ,, ,, 50° C	32.80	32.04	2.32

(1) Solutions which were 6*N* or lower with respect to HCl became turbid after exposure to the atmosphere and yielded after several hours standing blue precipitates which turned yellow after further exposure.

(2) Solutions which were 8*N* or higher in respect of HCl did not precipitate out tungstic acid and remained clear throughout the period of exposure but the blue colour characteristic of quinquevalent tungsten solutions faded gradually due to oxidation.

(3) Solutions in 10*N* HCl and kept under CO_2 remained practically stable for 14 days.

In connection with the above observations it seemed desirable to study the speed of oxidation of quinquevalent tungsten solutions by air or oxygen gas and to determine the order of the reaction. For this purpose either pure air or oxygen was passed at a rate of 200 bubbles per minute, at 25° C in 10*N* HCl solutions containing quinquevalent tungsten of normalities $7.7 \cdot 10^{-3}$ and $6.3 \cdot 10^{-3}$ when air and oxygen were bubbled respectively. Portions of the solutions were pipetted out every 30 minutes over a period of 4 hours and titrated against standard potassium dichromate. By plotting the logarithms of concentration against time in each series, a straight line was obtained indicating that the reaction was unimolecular and of the first order.

The formal potential of the W^{+6}/W^{+5} system

Collenberg and Guthe[7] gave 0.261 volt for the formal redox potential of the system W^{+6}/W^{+5} in concentrated hydrochloric acid. In order to obtain a

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more precise idea about the reducing power of quinquevalent tungsten, the formal redox potential of the system W^{+6}/W^{+5} was determined at different acidities by directly measuring the potential set when a bright platinum electrode was placed in a solution containing equimolecular quantities of W^{+6} and W^{+5} in hydrochloric acid of concentrations varying from 10.5 to 7*N*. At lower acidities the solutions became turbid unless phosphoric acid in appropriate quantities was added. The results as recorded in Table II show that the formal potential decreases with lowering the hydrochloric acid concentration. In the presence of H_3PO_4 of the same normality as HCl, on the other hand, the potential decreases slowly with declining acid concentration till 5.1*N* and then increases.

TABLE II

Normality of HCl	10.5		10.5	9.0	8.0		7.0
$E_f W^{+6}/W^{+5}$	0.247		0.216	0.155	0.108		0.065
Normality of H_3PO_4+HCl	6.7	5.1	3.4	1.88	1.3	0.99	0.5
$E_f W^{+6}/W^{+5}$	0.174	0.162	0.170	0.177	0.211	0.234	0.308

(i) *Determination of ferric iron*

Carter and Clews[8] gave values for the standard redox potential of the ferric-ferrous system in hydrochloric and phosphoric acid solutions of different normalities from which other values could be obtained by interpolation at the respective acidities. Thus in 0.5*N* HCl and 0.5*N* H_3PO_4 the redox potential amounts to 0.765 and 0.960 volt respectively. Taking the lower value to represent the formal redox potential in a solution which is 0.5*N* with respect to both HCl and phosphoric acid (the experimental value as obtained from Fig. 4 amounts to 0.7 volt) and 0.308 volt that of the W^{+6}/W^{+5} system under the same conditions *K*, the equilibrium constant of the reaction and α its degree of completion amount to $1.8 \cdot 10^{-8}$ and $1.34 \cdot 10^{-4}$ respectively. In 8*N* HCl the redox potential of the Fe^{+3}/Fe^{+2} system as obtained by interpolation amounts also to 0.790 volt. From this value and the formal redox potential of the W^{+6}/W^{+5} system at the same acid concentration which amounts to 0.108 volt, *K* and α amount to $2.8 \cdot 10^{-12}$ and $1.7 \cdot 10^{-6}$ respectively. The values of *K* and α so obtained indicate that the reaction between ferric iron and quinquevalent tungsten can be performed quantitatively under the above set of conditions. In Table III are shown some representative results of titrations of ferric iron with quinquevalent tungsten solution under a variety of conditions.

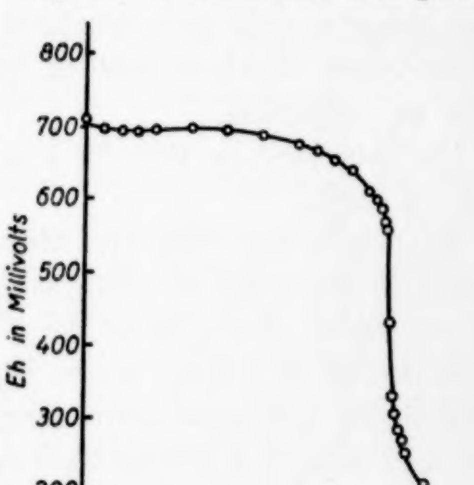

Fig. 4. Titration of 0.0172 *N* Fe^{+3} with 0.020 *N* W^{+5}.

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TABLE III

						Time for equilibrium near end point	mg Fe present	mg Fe found	Error %
Fe^{+3}	in	10N	HCl	at	25° C	18-20 min	9.64	9.68	0.41
,,	,,	,,	,,	,,	,,	,,	7.71	7.76	0.64
,,	,,	,,	,,	,,	,,	,,	5.87	5.82	0.78
,,	,,	,,	,,	,,	80° C	1-2 min	3.88	3.90	0.59
,,	,,	,,	,,	,,	,,	,,	1.95	1.94	0.5
,,	,,	,,	,,	,,	,,	,,	0.97	0.97	nil
,,	,,	1.8N	,,	,,	25° C	25-30 min	6.15	5.65	8.1
,,	,,	2.4N	,,	,,	,,	,,	6.15	5.73	6.79
,,	,,	8N	,,	,,	,,	18 min	5.697	5.699	0.04
,,	,,	0.3N	,,	,,	80° C	5-10 min	3.94	3.90	1.44
,,	,,	1.1N	,,	,,	,,	,,	1.70	1.71	0.52
,,	,,	0.5N	,,	,,	,,	,,	0.892	0.887	0.5
,,	,,	,,	,,	,,	,,	,,	0.563	0.570	1.2
,,	,,	0.5N	,,	,,	H_3PO_4 at 80° C	1-2 min	9.62	9.62	nil.
,,	,,	,,	,,	,,	,, ,, ,,	,,	7.75	7.76	0.13
,,	,,	,,	,,	,,	,, ,, ,,	,,	5.82	5.82	nil.
,,	,,	,,	,,	,,	,, ,, ,,	,,	3.88	3.88	nil.

The above results show that the best conditions for performing the titrations in presence of HCl alone are those in which the acid concentration is 8-10N and when the titration is conducted at 80° C. Under these conditions the equilibria are attained within one minute and the titration curves characterised with sharp inflections at the end point. At 25° C and at 8-10N HCl the equilibria are attained but slowly. This was also the case at lower acid concentrations and although the curves manifested sharper inflections at the end points, the errors were considerable, due apparently to the precipitation of tungsten trioxide. Better results could be obtained at lower acidities when the titration was performed at 80° C and more particularly when phosphoric acid was added. Under these latter conditions, the curves were smooth and characterised by sharp inflections at the end points.

The titration of ferric iron can also be performed visually since a blue colour appears at the end point. In absence of phosphoric acid, the blue colour appears only when the titration is made at 25° C and after about 0.2 ml of the reagent in excess of the theoretical quantity is added. A more precise visual titration can be performed in the presence of sulphocyanide.

(ii) *Determination of cupric copper*

The redox potential of the Cu^{+2}/Cu^{+} couple amounts to 0.16 volt as compared with 0.460 volt for the system $Cu^{+2}/CuCl_2^-$ at 25° C. Cupric ions are, therefore, only liable to be reduced by quinquevalent tungsten solutions if the product of the reduction was the complex anion $CuCl_2^-$. Since this can only be the case at higher hydrochloric acid concentrations, it was tried to perform the titrations in the presence of 8*N* HCl. Taking 0.460 volt to represent E_f for the system $Cu^{+2}/CuCl_2^-$ and 0.108 volt that of the W^{+6}/W^{+5} system, the degree of completion of the reaction amounts to $1.04 \cdot 10^{-3}$. The degree of completion is probably much lower since E_f as evaluated from the curves in Figs. 5 and 6 amounts to ∿ 0.55 volt and this corresponds to a degree of completion amounting to $1.8 \cdot 10^{-4}$, indicating that the reaction proceeds quantitatively to its end point. In Table IV are recorded some representative results.

TABLE IV

	mg Cu present	mg Cu found	Error %
Cu^{+2} in 8*N* HCl at 25° C ,, ,, H_3PO_4 alone	no inflection		
,, ,, 4*N* HCl + 0.5*N* H_3PO_4 at 80° C	6.357	6.337	0.31
,, ,, ,, ,, ,, ,, ,, ,,	12.714	12.681	0.26
,, ,, 8*N* ,, at 80° C	6.357	6.357	nil.

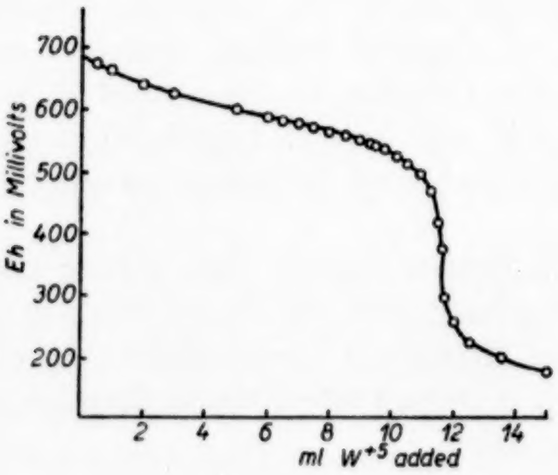

Fig. 5. Titration of 0.020*N* $CuSO_4$ in HCl + H_3PO_4 with 0.0172*N* W^{+5}.

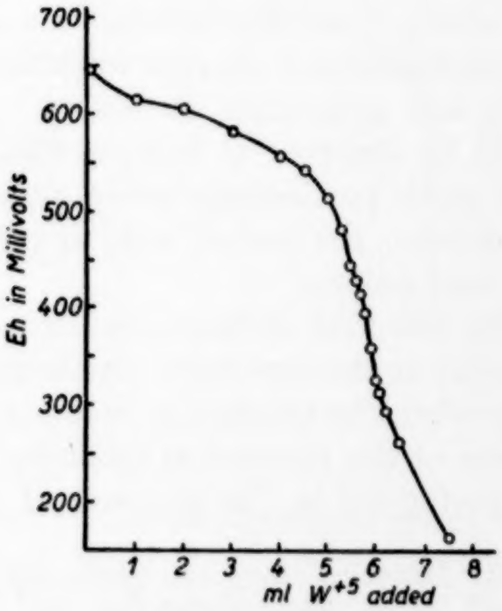

Fig. 6. Titration of 0.020*N* $CuSO_4$ in HCl with 0.0171*N* W^{+5}.

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The results show that reliable values are obtained when the titrations are performed at 80° C in presence of 8*N* HCl.

(iii) *Determination of iodate*

On account of its instability in strong acid media no formal potential values for the system IO_3^-/I^- are available. In predicting the reducibility of iodate by quinquevalent tungsten use was made of the E_0 value as calculated from thermal or entropy data and which amounts to 1.085 volt[9]. From the calculated degree of completion which amounts to $3.9 \cdot 10^{-14}$ and $4.3 \cdot 10^{-13}$ at 5*N* HCl respectively at 1*N* H_3PO_4, it is concluded that iodate can quantitatively oxidise quinquevalent tungsten.

Trials were now made to reduce iodate with quinquevalent tungsten in presence of varying quantities of hydrochloric acid or phosphoric acid and to reverse the process by using the iodate as the titrant whereby the quinquevalent tungsten solutions were admixed with different amounts of hydrochloric and phosphoric acids alone or together with mercuric or potassium chloride. The titrations were conducted potentiometrically, but alternately for comparison well-known volumetric procedures were carried out, involving the use of chloroform as a solvent for the liberated iodine. Some of the results obtained under the above conditions are given in Table Va and Vb.

TABLE Va

	Normality of iodate present	Normality of iodate found
0.001*M* IO_3^- in 2.8*N* H_3PO_4 at 25° C	0.0040	0.0047
,, ,, ,, ,, 3.6*N* ,,	0.0040	0.0044
,, ,, ,, ,, 5.2*N* ,,	0.0040	0.0041
,, ,, ,, ,, 2.0*N* HCl	0.0040	0.0039
,, ,, ,, ,, 5.0*N* ,,	0.0040	0.0023

TABLE Vb

	Normality of W^{+5} present $\times 10^3$	Normality of W^{+5} found $\times 10^3$	Error %
W^{+5} in 5*N* HCl + 1.6*N* H_3PO_4	6.25	6.24	0.16
,, ,, ,, ,, + 0.3*N*	6.25	6.24	0.16
,, ,, ,, ,, + 1*N* ,, + 20 ml $HgCl_2$ sat.	6.25	6.24	0.16
,, ,, sat. with KCl	6.25	6.24	0.16

From the results so obtained it becomes apparent that the reduction of iodate through quinquevalent tungsten in presence of phosphoric acid alone yields a mixture of iodine and iodine monochloride. The quantity of iodine decreases as

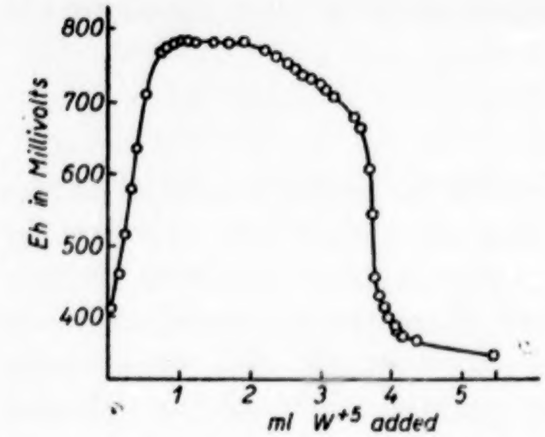

Fig. 7. Titration of 0.001 *M* KIO_3 with 0.0125 *N* W^{+5}.

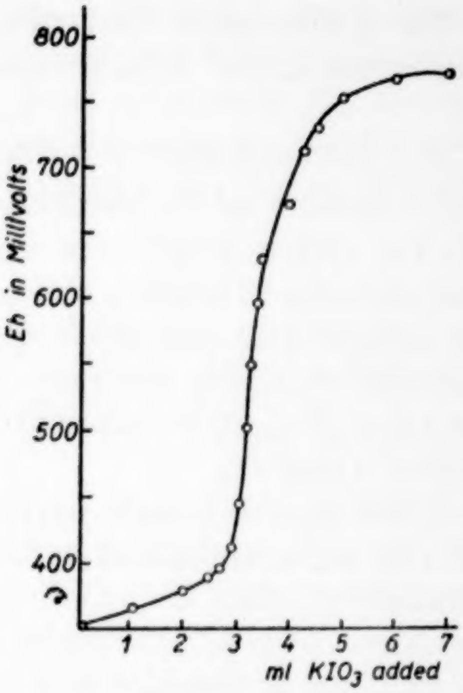

Fig. 8. Titration of 0.00625 *N* W^{+5} with 0.100 *M* KIO_3.

the concentration of phosphoric acid increases. Under these conditions the titration curves (Fig. 7) are characterised by an initial rise in potential followed by a slow decrease till the end point is reached. In presence of 2*N* HCl the reduction does not proceed quantitatively apparently due to the decomposition of some iodate and this becomes more pronounced the higher the concentrations of the acid are.

The reverse process of titrating quinquevalent tungsten with iodate under a variety of conditions as recorded in table Vb, leads exclusively to iodine monochloride[11]. A representative titration curve is shown in Fig. 8. The accuracy of the titration affords an additional method for standardising quinquevalent tungsten under the appropriate conditions.

SUMMARY

Quinquevalent tungsten prepared by the electrolytic reduction of tungstate in 10*N* HCl is sufficiently stable when kept in strong acid solutions under CO_2 to be used as an effective reducing agent in potentiometric titrations. It can be accurately standardised with dichromate. The formal redox potentials of the W^{+6}/W^{+5} system as determined at different acidities indicate that quinquevalent tungsten is more reducing than the corresponding molybdenum compound.

Quinquevalent tungsten can be applied successfully as a volumetric reagent in the potentiometric titration of ferric iron in 8-10*N* HCl or in a mixture of HCl and H_3PO_4 0.5*N* each and of cupric copper in 8*N* HCl at 80° C. It can also be applied for the estimation of iodate, provided that the latter is used as the titrant.

RÉSUMÉ

Le tungstène pentavalent, préparé par réduction électrolytique d'un tungstate dans l'acide chlorhydrique 10*N*, est assez stable pour être employé comme réducteur efficace dans les titrations potentiométriques, s'il est conservé dans une solution fortement acide sous CO_2. Il peut être titré exactement avec un bichromate. Les potentiels d'oxydo-réduction du système W^{+6}/W^{+5}, déterminés à divers degrés d'acidité, indiquent que le tungstène pentavalent est plus réducteur que le molybdène (V). Le tungstène (V) peut être utilisé avec succès comme réactif volumétrique pour le titrage potentiométrique du fer trivalent dans HCl 8-10*N* ou dans un mélange de HCl 0.5*N* et H_3PO_4 0.5*N*, et pour le dosage du cuivre bivalent dans HCl 8*N* à 80° C. Il peut aussi être appliqué à la détermination des iodates, à condition que ces derniers soient employés comme titrants.

ZUSAMMENFASSUNG

Fünfwertiges Wolfram, durch elektrolytische Reduktion von Wolframat in 10 *N* HCl hergestellt, ist genügend stabil, wenn es in stark sauren Lösungen unter CO_2 gehalten wird, um als wirksames Reduktionsmittel für potentiometrische Titrierung verwendet zu werden. Die formalen Reduktions-Oxidations-Potentiale des W^{+6}/W^{+5} Systems, bei verschiedenen Säuregraden gemessen, zeigen, dass fünfwertiges Wolfram mehr reduzierend wirkt als die entsprechende Molybdän-Verbindung.

Fünfwertiges Wolfram kann mit Erfolg als volumetrisches Reagenz für die potentiometrische Titrierung von dreiwertigem Eisen in 8-10*N* HCl oder in einer Mischung von 0.5*N* HCl und 0.5*N* H_3PO_4 und von zweiwertigem Kupfer in 8*N* HCl bei 80° C gebraucht werden. Es kann auch für die Bestimmung von Iodat verwendet werden, wenn das letztere als Titrant gebraucht wird.

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POTENTIOMETRIC TITRATION OF MILLIGRAM QUANTITIES OF URANIUM IN THE PRESENCE OF IRON

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Milligram quantities of uranium can be determined by semimicro titration of uranium(IV) with ceric sulfate, potassium dichromate or potassium permanganate[1]. The reduction of uranium(VI) with a slight excess of chromous sulfate followed by a potentiometric titration of the uranium(IV) with standard ceric sulfate in an atmosphere of carbon dioxide has been employed successfully in this laboratory. This method cannot be used in the presence of iron at room temperatures, however, since the iron is reduced to Fe(II) and titrated along with the uranium. At a higher temperature (about 60° C) the iron does not interfere, but the difficulty of working with small volumes at elevated temperatures makes such a procedure impractical.

This interference can be overcome at room temperatures by complexing the Fe(II) with 1,10-phenanthroline. The oxidation potential of the Fe(II)-Fe(III) system is thus changed, and the iron no longer interferes with the titration of the uranium(IV).

EXPERIMENTAL

A description follows of the reagents, apparatus and procedure used.

Reagents Standard ceric sulfate solution, approximately 0.1*N*. Slowly add 30 ml concentrated H_2SO_4 to 500 ml water with constant stirring. To this add 63 g $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$, stir to dissolve, cool, filter if turbid and dilute to 1 liter. Standardize against arsenious oxide. Ammonium hexanitratocerate cannot be used for the preparation of this reagent because of nitrate interference.

Chromous sulfate solution, approximately 10%. Prepare a 10% solution of potassium chromic sulfate and pour it through a Jones reductor filled with amalgamated zinc. Store the resulting chromous sulfate under a carbon dioxide atmosphere.

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1,10-*Phenanthroline solution,* approximately 0.25 g/ml. Suspend 2.5 g of 1,10-phenanthroline in 10 ml of water. Add 6*M* sulfuric acid dropwise with stirring until the reagent is completely dissolved.

Apparatus

Titration vessel. A flat-bottomed tube, 15 cm tall and 2 cm in diameter, fitted with a sidearm positioned so as to admit carbon dioxide gas above the solution.

Titrator. A Precision-Dow Recordomatic Titrator modified for semimicro titrations by replacing the 50-ml syringe buret with a 0.5-ml syringe buret.

Electrodes. (a) Reference Electrode. A straight platinum wire (20 gauge, 7 in. length) sealed into the buret containing the standard ceric sulfate solution. (b) Indicator Electrode. A straight gold wire (12 gauge) which dips into the solution being titrated to a depth of approximately 5 mm. A gold indicator electrode was preferred to platinum because platinum appeared to catalyze the Cr(II)-Cr(III) oxidation by H^+ ion. For best results the gold electrode should be cleaned after each titration by dipping into a chromic acid cleaning mixture and rinsing thoroughly with distilled water.

Procedure

The nitrate-free solution is placed in the titration vessel, 50 λ of concentrated (36*N*) sulfuric acid added, and the volume adjusted to about 2 to 4 ml. A stream of carbon dioxide gas is maintained over the sample, and the solution stirred magnetically, during the entire titration, using a 3/8 inch glass-covered nickel wire stirrer. Chromous sulfate is added slowly from a 50 λ micro pipet until the potential indicates complete reduction of the U(VI) to U(IV). The ceric sulfate feed is then turned on, and the titration continued until the Cr(II)-Cr(III) oxidation is complete. At this point 12.5 mg of 1,10-phenanthroline (50 λ of the above solution) is added for each 0.1 mg of iron present.

The 1,10-phenanthroline must not be added prior to the oxidation of the Cr(II) since it also forms a stable complex with this ion. The titration is continued until a second break in potential (the U(IV)-U(VI) break) is obtained. The instrument is standardized by determining the distance of chart travel in inches equivalent to the milligrams of uranium in a standard uranyl sulfate solution, *i.e.,* the distance between the Cr(II)-Cr(III) break and the U(IV)-U(VI) break is measured. The quantity of uranium represented by one inch of chart is calculated and is used as a factor to calculate the amount of uranium in an unknown sample. For example: a standard sample containing 2.00 mg of U gave 7.10 inches of chart travel between the breaks which is equivalent to $\frac{2.00}{7.10} = 0.282$ mg U per inch of chart travel. An unknown gave 8.45 inches of chart travel between breaks and therefore contained $8.45 \times 0.282 = 2.38$ mg uranium. A sample titration curve is shown in Fig. 1.

Results

The above procedure was used to determine milligram quantities of uranium in the presence of various amounts of iron impurity. The results are given in Table I.

DISCUSSION

A precision and accuracy of about 1% can be obtained with samples containing only uranium and iron as metallic constituents.

Other non-reducible cations (aluminum, nickel, etc.) do not interfere although their presence may cause a slight decrease in the accuracy of the method.

The method does not work successfully for the analysis of samples containing much more than one milligram of iron, even if a correspondingly larger amount of 1,10-phenanthroline is added.

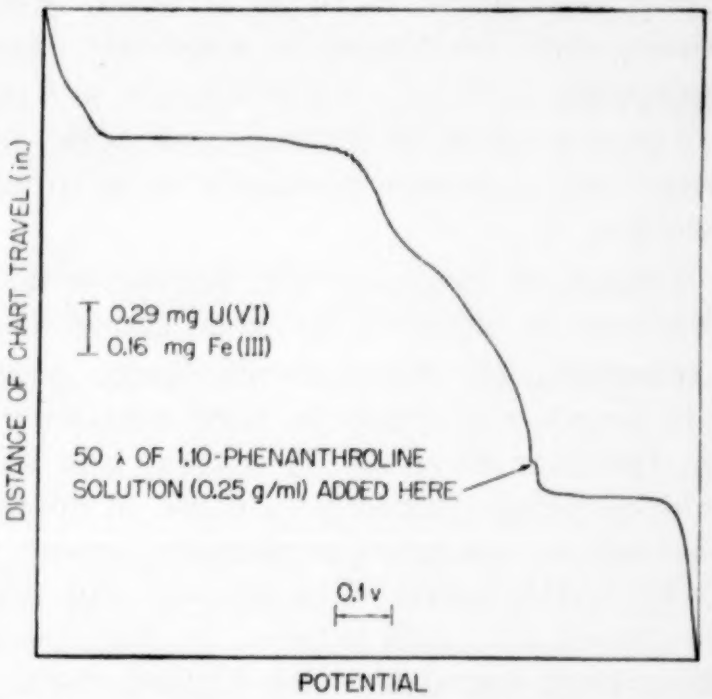

Fig. 1. Potentiometric titration of uranium(IV)

TABLE I

DETERMINATION OF URANIUM IN PRESENCE OF IRON

Sample	Fe added (mg)	1,10-Phenanthroline added (mg)	U (mg) taken	U (mg) found	*d*
1	0.125	25	2.53	2.51	0.05
2	0.250	25	2.53	2.54	0.02
3	0.370	25	2.53	2.56	0.00
4	0.500	25	2.53	2.62	0.06
5	0.250	63	2.53	2.53	0.03
6	1.00	63	2.53	2.61	0.05
7	1.00	125	2.53	2.56	0.00
			Mean =	2.56	$\Sigma d = 0.21$

Average deviation of single measurement $= \frac{0.21}{7} = 0.030$ per cent. absolute.

$$= \frac{0.030}{2.56} \cdot 100 = 1.17\%$$

8	1.00	125	1.76	1.79	
9	1.00	125	0.51	0.51	

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SUMMARY

A method is described for the potentiometric titration of milligram quantities of the uranium(IV) ion in the presence of iron. This is accomplished by complexing the iron with 1,10-phenanthroline. The uranium can then be titrated with standard ceric sulfate without interference from the iron.

RÉSUMÉ

On donne une méthode de détermination potentiométrique de l'uranium(IV) pour des quantités de l'ordre du milligramme, en présence d'un sel de fer. Le fer est complexé par la 1,10-phénanthroline. Puis on détermine l'uranium par titration avec une solution étalon de sulfate de cérium. Le fer n'intervient pas au cours de la titration et ne gêne pas.

ZUSAMMENFASSUNG

Eine Methode für die potentiometrische Bestimmung von Milligrammengen Uranium(IV) in Mischungen mit Eisen(II) wird beschrieben. Diese Methode besteht in der Komplexbildung von Eisen mit 1,10-Phenanthrolin. Das Uranium kann dann ohne Störung durch das Eisen mit standardisiertem Ceriumsulfat titriert werden.

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PRÉVISION DES COURBES DE DOSAGES POTENTIOMÉTRIQUES

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DÉFINITIONS ET CONVENTIONS

Dans un précédent mémoire[1], nous avons montré comment la connaissance des courbes de polarisation permettait d'interpréter les résultats expérimentaux observés au cours des déterminations de potentiels d'oxydo-réduction.

Dans ce mémoire, nous nous proposons, à l'aide des courbes de polarisation, d'interpréter les phénomènes observés au cours des titrages potentiométriques.

Au préalable, nous rappelons un certain nombre de définitions et de conventions que nous utiliserons par la suite.

Courbes de l'eau — Classification des oxydants et des réducteurs

L'eau peut être considérée soit comme oxydant, soit comme réducteur et il est possible de tracer les courbes de polarisation correspondantes sur une électrode inattaquable.

Il est possible de classer relativement à une électrode donnée les oxydants et les réducteurs en trois catégories par rapport à l'eau:

Dans le cas des oxydants (zone cathodique) citons d'abord ceux qui réagissent chimiquement sur l'eau et par conséquent, n'existent pas en solution aqueuse, comme par exemple le fluor. Pour d'autres, la courbe de polarisation se situe à des potentiels supérieurs à ceux de la courbe de réduction de l'eau comme le fer ferrique[2]. Enfin, ceux dont la courbe se trouverait au-delà de la courbe de réduction de l'eau comme le tétrathionate[3].

On raisonnerait de la même façon en ce qui concerne les réducteurs (zone anodique). Il est alors possible de définir quatre régions (Fig. 1) dépendant de la nature de l'électrode:

Région I: réducteurs dont on peut tracer la courbe de polarisation.
Région II: réducteurs dont on ne peut pas tracer la courbe de polarisation.
Région III: oxydants dont on peut tracer la courbe de polarisation.
Région IV: oxydants dont on ne peut pas tracer la courbe de polarisation.

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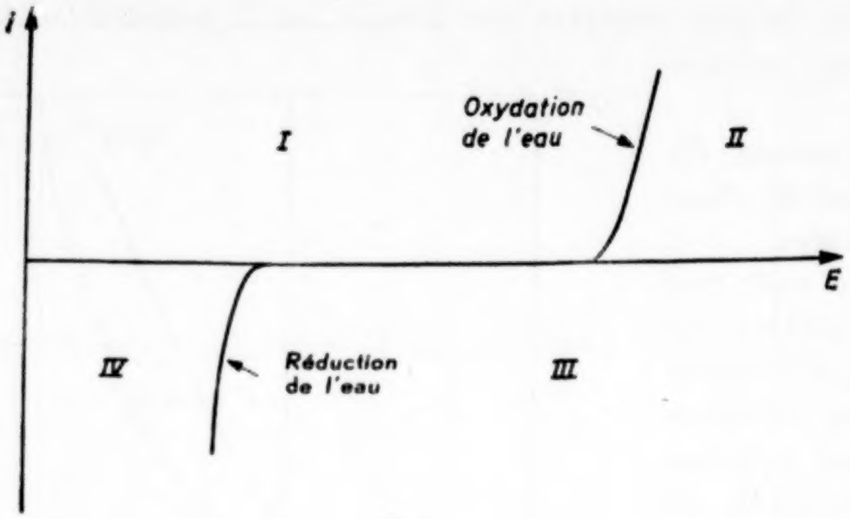

Fig. 1

Nous dirons qu'un corps (molécule ou ion) est électroactif vis-à-vis d'une électrode donnée, lorsqu'il est possible de tracer directement la courbe de polarisation correspondante sur l'électrode envisagée. En se reportant au schéma précédent (Fig. 1), les réducteurs électroactifs se situent dans la région I et les oxydants dans la région III.

Potentiel d'une électrode électriquement isolée

Considérons une solution contenant différents corps électroactifs ne réagissant pas chimiquement ou tout au moins très lentement. Plongeons une électrode dans cette solution. Elle prend un potentiel mixte[4,5] *instantané* tel que la somme des intensités anodiques soit égale à la somme des intensités cathodiques puisqu'il ne peut pas y avoir de courant. Ce qui revient à dire qu'à un instant donné l'échange d'électrons par l'intermédiaire de l'électrode est un état de régime: si en une seconde l'ensemble des réducteurs présents en solution cède n électrons à l'électrode, celle-ci en fournit n pendant le même temps à l'ensemble des oxydants.

Dans ce bilan, il faut faire intervenir la courbe de polarisation de chaque corps électroactif relativement à l'électrode envisagée. L'eau peut intervenir soit comme oxydant soit comme réducteur.

FORME DES COURBES DE DOSAGE EN DEHORS DU POINT EQUIVALENT

Lorsque les formes réduite et oxydée d'un système rédox sont électroactives, le potentiel pris par une électrode inattaquable plongée dans une solution contenant les deux formes est donné par la formule de NERNST:

$$E = E_\circ + \frac{RT}{nF}\log\frac{|\mathrm{Ox}|}{|\mathrm{Red}|}$$

et le potentiel croit quand la concentration de l'oxydant augmente ou quand celle du réducteur diminue.

Par contre, si une des formes n'est pas électroactive, l'électrode indique un

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potentiel mixte; on peut observer une *diminution de potentiel lorsqu'on ajoute un oxydant à une solution réductrice.*

Prenons l'exemple du dosage classique du thiosulfate par l'iode:

Si l'on trace avec une électrode de platine les courbes de polarisation d'une solution d'iodure 0.1*M* et d'une solution de thiosulfate 0.1*M* en milieu acétique (pH = 5.53), le potentiel à courant nul de la première E_1 est inférieur d'environ 50 mV à celui de la seconde E_2 (Fig. 2).

Lorsqu'on ajoute de l'iode à une solution de thiosulfate, il apparaît quantitativement de l'iodure selon la réaction:

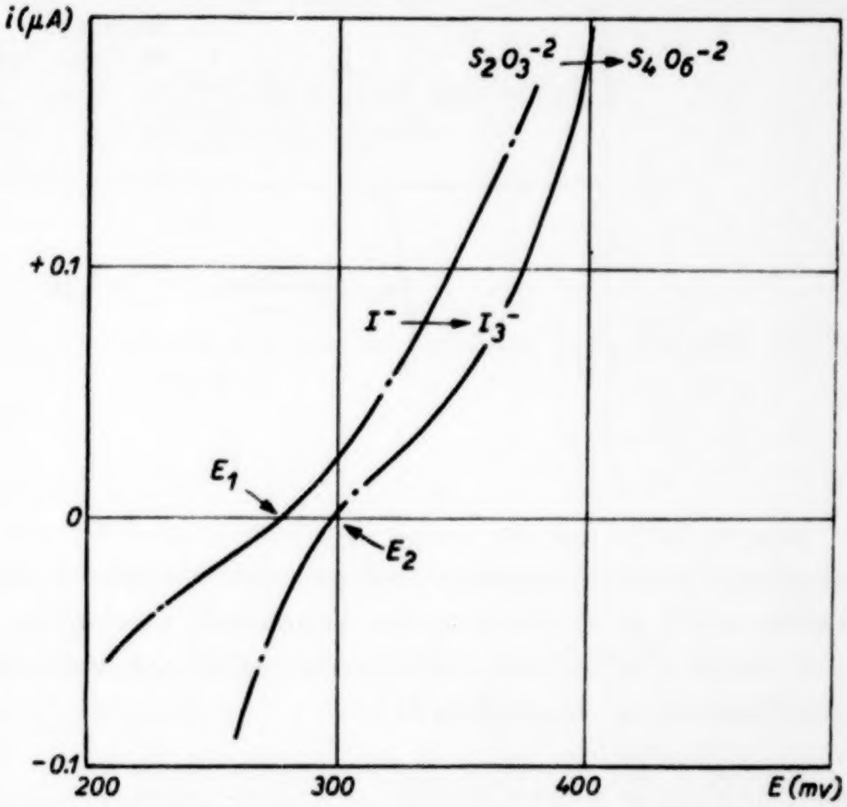

Fig. 2. Courbes de polarisation des ions $S_2O_3^{-2}$ et I^- vis-à-vis d'une électrode de platine.

$$2\ S_2O_3^{-2} + I_2 \rightleftharpoons S_4O_6^{-2} + 2\ I^-$$

Or, le tétrathionate n'est pas électroactif sur une électrode de platine poli[3]. Donc, avant le point équivalent, seuls les deux réducteurs $S_2O_3^{-2}$ et I^- interviennent pour fixer un potentiel à l'électrode et celui-ci est fixé par le réducteur dont la courbe de polarisation se situe aux potentiels les plus bas[1]. Dans le cas présent, l'iodure apparaissant au cours du dosage, le potentiel doit donc diminuer au fur et à mesure de l'addition d'iode, puis augmenter du fait de la dilution et lorsqu'une trace d'iode est présente en solution c'est-à-dire un peu avant le point équivalent.

La courbe de dosage obtenue en oxydant 20 ml d'une solution de thiosulfate 0.0995*N* par une solution d'iode 0.1036*N* est représentée Fig. 3. Les indications de l'électrode de platine variant au cours du temps, avant chaque nouvelle addition de réactif, nous attendons que la variation de potentiel soit inférieure à 1 mV pendant 10 minutes.

Nous avons obtenu des résultats analogues lors du dosage de As(III) par l'iode à pH 8 avec une électrode de graphite (Fig. 4).

ÉTUDE DES COURBES DE DOSAGE AU POINT ÉQUIVALENT

Si l'on suit par la méthode potentiométrique classique le dosage du réducteur d'un premier système:

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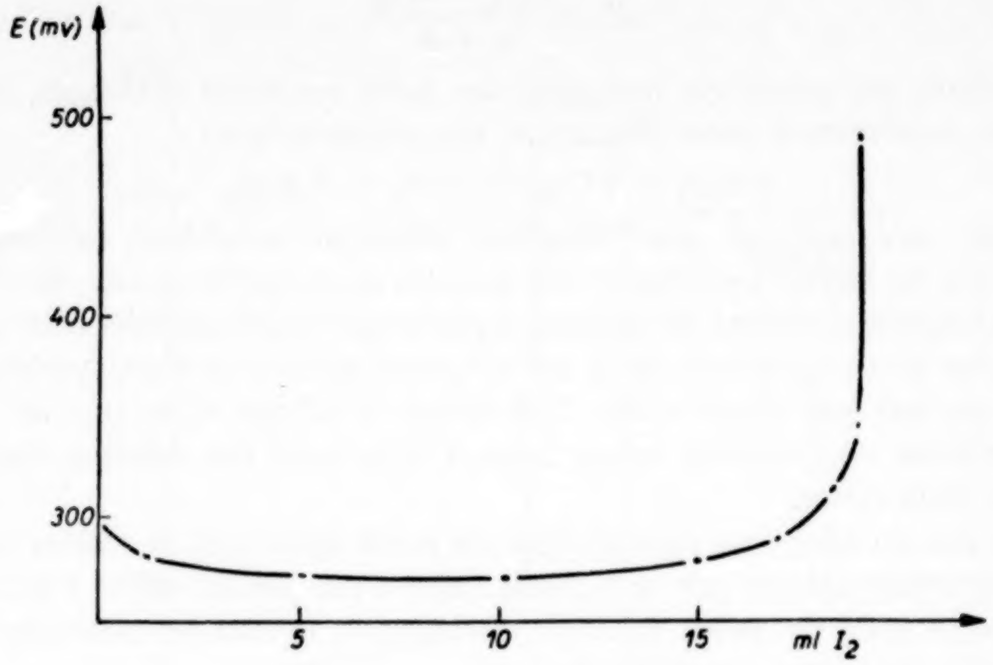

Fig. 3. Courbe de dosage du thiosulfate par l'iode.

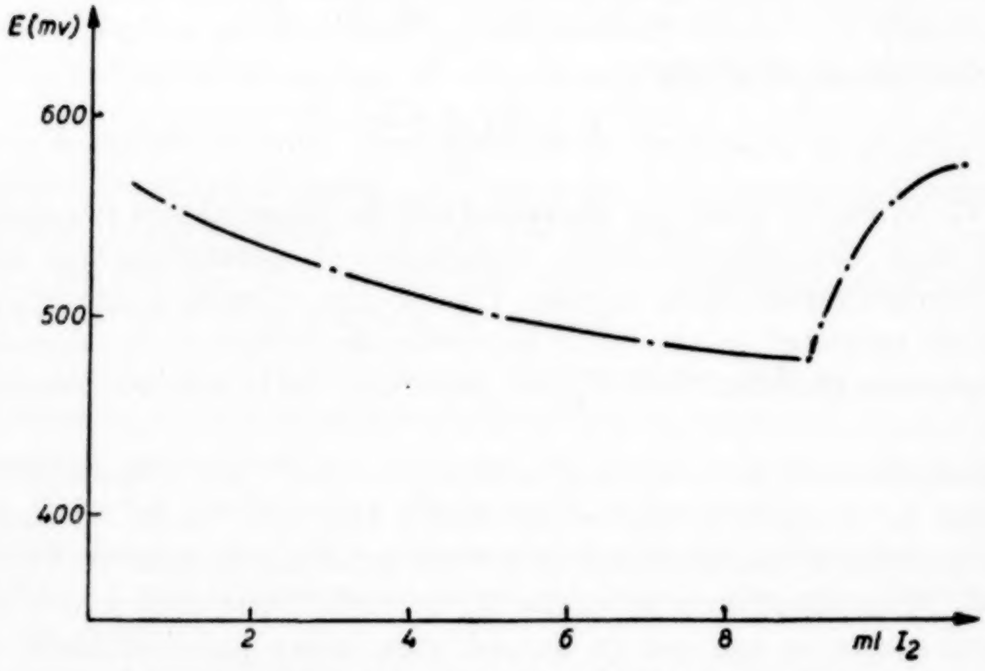

Fig. 4. Courbe de dosage de As(III) par l'iode.

$$\mathrm{Red}_1 \rightleftharpoons \mathrm{Ox}_1 + n_1 e$$

par l'oxydant d'un second:

$$\mathrm{Ox}_2 + n_2 e \rightleftharpoons \mathrm{Red}_2$$

un calcul classique (voir par exemple 6) montre que le potentiel du point équivalent est:

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$$E = \frac{bE_1 + aE_2}{a + b}$$

E_1 et E_2 étant les potentiels normaux des deux systèmes envisagés, *a* et *b* les coefficients intervenant dans l'équation stoechiométrique:

$$a\,\mathrm{Red}_1 + b\,\mathrm{Ox}_2 \rightleftharpoons a\,\mathrm{Ox}_1 + b\,\mathrm{Red}_2$$

Toutefois, ceci suppose que l'équilibre *chimique* précédent est rapidement atteint et que les formes oxydées et réduites des deux systèmes sont électroactives puisque la formule ci-dessus est obtenue à partir de l'équation de NERNST appliquée à chacun des deux systèmes. Or il est fréquent qu'un ion d'un système oxydo-réducteur ne soit pas électroactif. L'électrode n'indique alors pas un potentiel d'équilibre mais un potentiel mixte faisant intervenir des données cinétiques à l'électrode indicatrice.

Dans ce cas, en adoptant pour abcisse du point équivalent la valeur correspondant au potentiel calculé par la formule précédente l'écart entre l'abcisse ainsi déterminée et celle du point équivalent chimique (quantités stoechiométriques des réactifs) peut être considérable.

Nous allons décrire le cas du dosage du fer ferreux, par le permanganate, les résultats étant caractéristiques. Le système Fe(III)/Fe(II) a un potentiel calculé $E_1 = 0.77$ V[7]. Celui du système MnO_4^-/Mn(II) est $E_2 = 1.52$ V[7]. Le potentiel du point équivalent théorique

$$E = \frac{E_1 + 5E_2}{6}$$

est 1.395 V. Or Mn(II) n'est pas électroactif et le potentiel pris par une électrode de platine dans une solution d'ions manganeux et permanganique ne dépend que de la concentration de ce dernier. C'est-à-dire, d'après notre hypothèse, on détermine un potentiel mixte entre la courbe de réduction du permanganate et celle d'oxydation de l'eau. Soit E_M ce potentiel; on a nécessairement $E_M < E_2$ (1 p. 90).

Expérimentalement nous avons trouvé $E_M = 1.40$ V à la concentration $0.02N$.

Remarque. Le dosage est effectué en milieu H_2SO_4N. Le fer ferrique est alors partiellement complexé et le potentiel normal apparent du système Fe(III)/Fe(II) est abaissé. Nous adopterons la valeur $E_1 = 0.68$ V que nous avons déterminée expérimentalement et qui est en accord avec celles précédemment obtenues[8]. Avec cette nouvelle valeur, le potentiel du point équivalent théorique est abaissé de 15 mV.

La courbe de neutralisation de 20 ml d'une solution de sel de Mohr $0.01582N$ par une solution de permanganate $0.1098N$ est représentée Fig. 5.

En prenant pour abcisse du point équivalent la valeur déterminée à partir des potentiels d'équilibre, on fait une erreur de 20% par excès.

Le point équivalent chimique a lieu au saut de potentiel comme l'a déjà mentionné en particulier MÜLLER[9].

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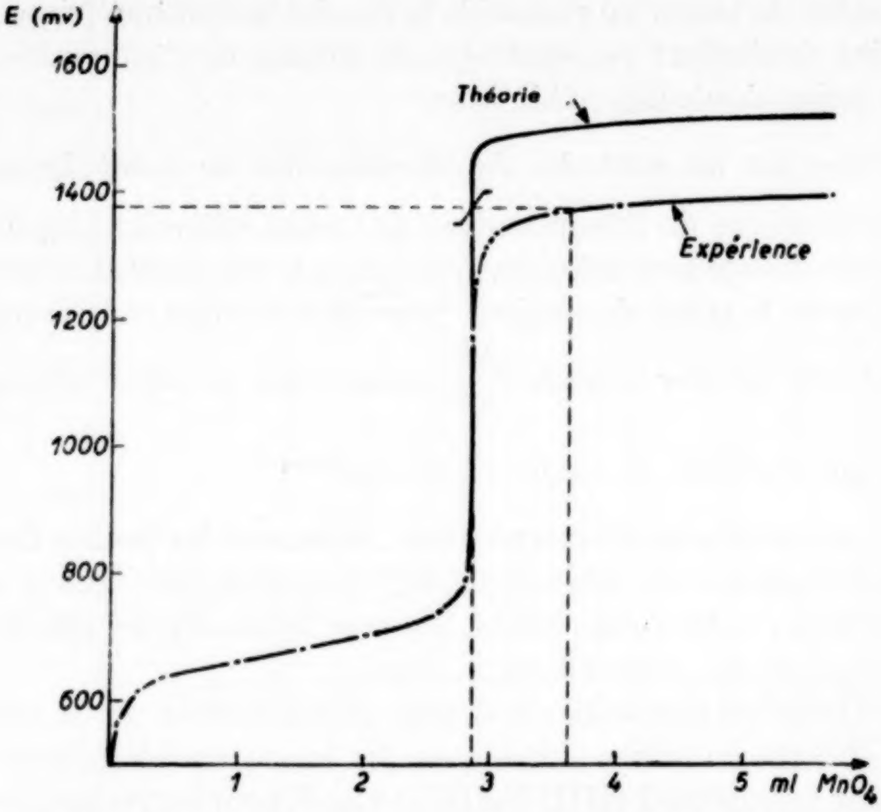

Fig. 5. Courbe de dosage du fer ferreux par le permanganate.

Remarque I. Avant le point équivalent deux électrodes de platine poli indiquent le même potentiel à moins de 1 mv près et la courbe théorique coïncide avec la courbe expérimentale. Au delà l'écart entre les deux électrodes peut atteindre 20 mV ce qui prouve bien que celles-ci indiquent un potentiel mixte dépendant en particulier de leur état de surface.

Remarque II. Entre les potentiels 0.85 V et 1.25 V les indications des électrodes peuvent differer de 100 mV et les potentiels varient rapidement au cours du temps.

Le phénomène précédemment envisagé est général: lorsque dans un dosage un seul ion d'un des systèmes est électroactif, si l'on adopte pour potentiel du point équivalent celui calculé à partir des potentiels d'équilibre, on obtient systématiquement une erreur par excès ou par défaut selon que l'ion électroactif est titrant ou titré.

Nous l'avons observé également au cours des dosages suivants:

fer ferreux par bichromate
iode par thiosulfate
thiosulfate par iode

Remarque sur le choix d'un indicateur d'oxydo-réduction

Connaissant les potentiels d'équilibre du système titré et titrant, on peut à priori déterminer l'indicateur convenable pour le dosage envisagé.

D'après ce qui vient d'être dit, si un seul ion d'un des systèmes est électroactif,

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il est indispensable de tracer au préalable la courbe potentiométrique, le potentiel calculé du point équivalent pouvant être en dehors de l'intervalle de potentiel définissant le point équivalent chimique.

Remarque sur les méthodes de détermination du point équivalent

La méthode classique de détermination du point équivalent repose sur le fait qu'une courbe de dosage potentiométrique présente un point d'inflexion pouvant être confondu avec le point équivalent pour une réaction suffisamment quantitative. On peut soit calculer la pente $\frac{\Delta E}{\Delta V}$ passant par un maximum, soit la dérivée seconde $\frac{\Delta^2 E}{\Delta V^2}$ qui s'annule au point équivalent[6,10,11].

Mais toutes ces méthodes d'interpolation supposent les points figuratifs de la courbe potentiel-volume de réactif ajouté, parfaitement définis au voisinage du point équivalent. Cette remarque en diminue beaucoup les possibilités d'utilisation pratique, comme nous allons le voir.

Nous avons étudié en particulier le dosage du fer ferreux par le cérium cérique.

Celui-ci est effectué en milieu sulfurique $4N$; les potentiels normaux apparents sont 0.65 V pour le système Fe(III)/Fe(II) et 1.40 V pour le système Ce(IV)/Ce(III).

La courbe de dosage de 20 ml d'une solution de sel de Mohr $0.01582N$ par une solution de sulfate cérique $0.1072N$ est représentée Fig. 6. Au potentiel théorique du point équivalent

$$E = \frac{0.65 + 1.40}{2} = 1.025 \text{ V}$$

un calcul simple montre que les concentrations des ions ferreux et cérique sont toutes deux égales à $7 \cdot 10^{-9}$ ion-gramme/litre. Cette concentration est bien inférieure aux concentrations limites des ions envisagés: au voisinage du point équivalent l'électrode n'est pas en équilibre avec les quatre corps. Elle indique un potentiel mixte fixé par les courbes de réduction du fer ferrique et d'oxydation du cérium céreux.

Dans la zone comprise entre 0.78 V et 1.35 V (Fig. 6) les indications de deux électrodes de platine poli diffèrent. L'écart entre celles-ci passe par un maximum, au voisinage du point équivalent (l'écart maximum que nous avons observé est d'environ 40 mV). De plus, le potentiel d'une électrode n'est pas stable, il varie au cours du temps. Dans le tableau ci-dessous, sont indiquées les valeurs du potentiel pris par une électrode après addition de 2.975 ml de solution cérique, le point équivalent correspondant à un volume de 2.965 ml. L'instant auquel est introduit le réactif est pris comme instant initial.

30''	1.141
1'	1.153
1'30''	1.168
2'	1.179
2'30''	1.188

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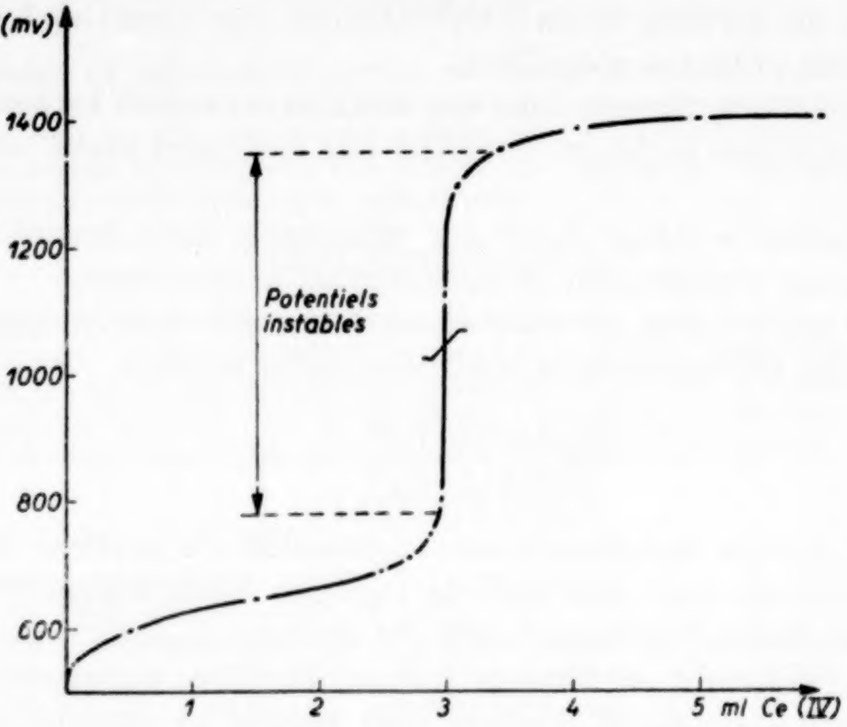

Fig. 6. Courbe de dosage du fer ferreux par le cérium cérique.

Enfin, l'agitation de la solution provoque une variation instantanée du potentiel.

En résumé, pour que les méthodes d'interpolation précédemment citées soient appliquables, il faut que:

— les formes oxydées et réduites des deux systèmes soient électroactives.

— la concentration de chacun des corps, au point équivalent, soit supérieure à sa concentration limite.

Ces conditions sont rarement réalisées au cours des réactions d'oxydo-réduction. En effet, souvent au moins un des systèmes a une forme non électroactive. Enfin, on sait[12] que pour obtenir une précision de 0.2% l'écart entre les potentiels d'équilibre doit être au moins égal à 0.32 V. En analyse les solutions à titrer sont en général 0.01M ce qui fait au point équivalent une concentration égale à $2 \cdot 10^{-5}M$. Cette dernière est presque toujours inférieure à la concentration limite du corps envisagé.

REMARQUE SUR LA DÉTERMINATION DES POTENTIELS D'OXYDO-RÉDUCTION — MÉDIATEURS

On sait qu'on appelle médiateur un système oxydo-réducteur fixant rapidement un potentiel à l'électrode et susceptible de se mettre rapidement en équilibre chimique avec un autre système dont on peut déterminer le potentiel (voir par exemple 13).

En tenant compte de la non-identité possible entre les mécanismes chimiques et électrochimiques, on peut interpréter simplement le rôle d'un médiateur et en préciser les limites d'utilisation.

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Considérons un système rédox (As(V)/As(III) par exemple) à faible densité de courant i_0 au potentiel d'équilibre.

Une électrode inerte plongée dans une solution contenant les formes oxydée et réduite de ce système prend un potentiel plus ou moins stable après un temps très long[14].

Soit un deuxième système (I_3^-/I^- par exemple) à forte densité de courant i_0, c'est-à-dire fixant instantanément un potentiel à l'électrode.

Il se trouve que ces deux systèmes se mettent *rapidement en équilibre chimique.* Les activités des différents corps sont liées par la relation:

$$\frac{|H_2AsO_4^-| \cdot |I^-|^3}{|HAsO_2| \cdot |I_3^-|} = K$$

et l'électrode indique instantanément le potentiel du système iode/iodure, les densités de courant dues aux ions de l'arsenic étant négligeables.

Mais ce potentiel est également celui du système: $H_2AsO_4^-/HAsO_2$ puisque les quatre formes présentes en solution sont en équilibre chimique.

Si les quantités d'iode et d'iodure sont faibles les concentrations des ions arsénique et arsénieux sont pratiquement inchangées et le potentiel mesuré est celui du système initial.

Choix d'un médiateur

Le système doit avoir une forte densité de courant i_0 à son potentiel d'équilibre. Il doit se mettre rapidement en *équilibre chimique* avec le système étudié. Il faut enfin que les potentiels des deux systèmes soient voisins. En effet, le médiateur est introduit en faible quantité dans la solution. Si les potentiels des deux systèmes sont trop éloignés, l'équilibre chimique est fortement déplacé dans un sens ou dans l'autre. La concentration de la forme oxydée ou réduite du médiateur est alors inférieure à sa concentration limite et on détermine le potentiel limite de la forme réduite ou oxydée du médiateur.

Dans le cas présent, le système iode/iodure ne peut servir de médiateur que dans un certain intervalle de pH comme l'a déjà signalé Foerster[15].

En effet, en milieu très acide, As(V) oxyde quantitativement l'iodure, par contre, en milieu neutre (pH = 8) As(III) réduit quantitativement l'iode, les potentiels d'équilibre des deux systèmes étant trop différents.

RÉSUMÉ

La connaissance des courbes de polarisation permet d'expliquer les faits observés au voisinage du point équivalent au cours des dosages potentiométriques ainsi que les anomalies présentées par certaines courbes de dosage.

Il est aussi possible d'interpréter le rôle d'un médiateur lorsqu'on effectue des déterminations de potentiels d'oxydo-réduction.

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SUMMARY

The knowledge of polarisation curves can be used to explain the facts observed in the neighbourhood of the equivalent point in the course of potentiometric determinations as well as the anomalies presented by certain determination curves. It is also possible to interpret the role of a "potential mediator" during the determinations of oxido-reduction potentials.

ZUSAMMENFASSUNG

Die Kenntnis der Polarisationskurven erlaubt die in der Nähe des Äquivalenzpunktes während potentiometrischer Bestimmungen beobachteten Tatsachen sowie die sich bei gewissen Bestimmungskurven zeigenden Anomalien zu erklären. Es ist ebenfalls möglich die Rolle eines ,,Potentialvermittlers" zu erläutern, wenn man Bestimmungen des Oxydations-Reduktionspotentials durchführt.

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THE POLAROGRAPHIC BEHAVIOUR OF SOME ELEMENTS IN CONCENTRATED CALCIUM CHLORIDE SOLUTION

IV. THE DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF METALLIC IMPURITIES IN CALCIUM METAL

by

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INTRODUCTION

Previous papers in this series[1,2,3] have described studies of the polarographic behaviour of copper, chromium, nickel, lead, cadmium, iron and manganese in $5M$ calcium chloride solution. This work had the ultimate object of developing a method for the determination of as many of these elements as possible when present as impurities in calcium metal.

The reason for the choice of a $5M$ solution as base electrolyte (that of increased sensitivity without the necessity of chemical concentration), has already been mentioned and the difficulties inherent in the use of a medium of such high viscosity and low water free energy have been discussed[1].

The work was carried out on a Randles-type cathode ray polarograph constructed in these laboratories[4,5] as this instrument is much more sensitive than conventional polarographs and is much more rapid in operation. The essential differences between the results of cathode ray methods and those of conventional polarography have been given in previous publications[1,5].

The European sign convention has been employed throughout this paper and the actual peak potential obtained on the cathode ray polarograph for each wave has been given. The difference between the cathode ray peak-potential and the conventional half-wave potential has been detailed elsewhere[1,5].

PRELIMINARY CONSIDERATIONS

The polarographic data of analytical importance are summarised in Table I. All pH values quoted in this table and throughout the paper refer to a solution that has been diluted tenfold, as pH values measured in $5M$ calcium chloride are almost meaningless[1].

The pH range for satisfactory determination of iron was considered to be too narrow for routine work and no attempt was therefore made to include a determination of this element in the method.

TABLE I

Element	Half-wave potential* (vs. N.H.E.)	Peak potential (Applied volts vs. Hg pool)	Satisfactory pH range	Reduction occurring
Copper	—0.085	—0.271	1—6	$Cu^{I} \rightarrow Cu$
Lead	—0.29	—0.476	1—7.5	$Pb^{II} \rightarrow Pb$
Chromium	—0.32	—0.506	1—3.5	$Cr^{III} \rightarrow Cr^{II}$
Nickel	—0.32	—0.506	1—6.5	$Ni^{II} \rightarrow Ni$
Cadmium	—0.56	—0.746	1—9	$Cd^{II} \rightarrow Cd$
Iron	—1.00*	—1.19*	3.5—4	$Fe^{II} \rightarrow Fe$
Manganese	—1.2	—1.386	5.0—7.5	$Mn^{II} \rightarrow Mn$

* Value varies somewhat with concentration of iron.

The data in Table I show that it is not possible to determine all the remaining elements by polarography of one solution. If two solutions are used, one of pH 1-2 and the other of pH 7.0-7.5 the chromium reduction wave will coincide with those of nickel and lead in the more acid medium. In the other solution, however, both chromium and nickel will be precipitated, allowing the lead to be determined. A correction for the contribution of lead to the combined step may then be made as it has been shown[2] that the waves of the three elements are fully additive, although the diffusion coefficients for lead in the two media are slightly different and must be allowed for.

Attempts to separate the chromium and nickel waves by complexing with oxalic acid, potassium oxalate, potassium cyanide, triethanolamine, ethylenediaminetetra-acetic acid and dimethylglyoxime were unsuccessful. Oxidation of the trivalent chromium to the hexavalent state with perchloric acid was tried and some success was achieved, a nickel-free chromium wave being obtained at pH 5-6. However, in view of the tedious nature of the oxidation and the very critical pH adjustment necessary, it was abandoned as unsuitable for inclusion in a rapid routine method. It was decided instead that either the chromium or nickel should be determined by a separate chemical method and that the other elements would be determined in the two $5M$ calcium chloride solutions already mentioned. Nickel was selected as the element for chemical determination as this was considered to be the simpler to carry out.

In view of the above considerations it was necessary to devise a simple procedure for the preparation of two aliquots of a $5M$ calcium chloride solution from calcium metal, one having a pH in the range 1-2 and the other in the range 6.5-7.5.

PREPARATION OF $5M$ CALCIUM CHLORIDE SOLUTIONS

The preparation of $5M$ calcium chloride solutions of any desired pH from $2.5M$ calcium chloride solutions has already been outlined in Part I of this series[1]

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and will be described in detail later in this paper. These solutions were prepared from calcium carbonate.

In the case of solutions prepared from calcium metal it was known that, although calcium metal itself dissolves easily in water and hydrochloric acid, some of the metallic impurities would not pass into solution under the conditions employed. It was, therefore, necessary to remove the residue for separate treatment.

In order to ensure complete precipitation of this insoluble material it was found to be necessary to allow the solution to stand overnight. The solution was then filtered and the filter paper ashed in a silica crucible before dissolution of the residue by heating with fuming perchloric acid. During dissolution precautions were taken against the loss of chromium as volatile CrO_2Cl_2. This was effected by carrying out the reaction in a boiling tube fitted with a "cold finger" condenser (Fig. 1).

The perchloric acid solution of the residue was added to the bulk of the calcium solution, which was then diluted to make the final concentration of calcium 2.5*M*. The polarographic analysis of the insoluble residue itself will be the subject of a paper to be published in the near future.

20 ml aliquots of the calcium solution were withdrawn and evaporated, some to dryness and others to 8 ml, 7 ml, 6 ml, etc. Water was then added to each aliquot to give a final volume of 10 ml. Only those aliquots which had been evaporated to dryness had a reproducible pH, but when solutions containing known amounts of impurities were treated in this manner low recoveries were obtained, due to the impurities being rendered insoluble. The evaporation was therefore taken to the stage when a solid white crust first appeared on the surface of the solution. This technique gave a reproducible pH while not affecting the solubility of the impurities. It was therefore adopted in the method, the requisite final pH being obtained by addition of standard amounts of acid or alkali before the dilution to 10 ml.

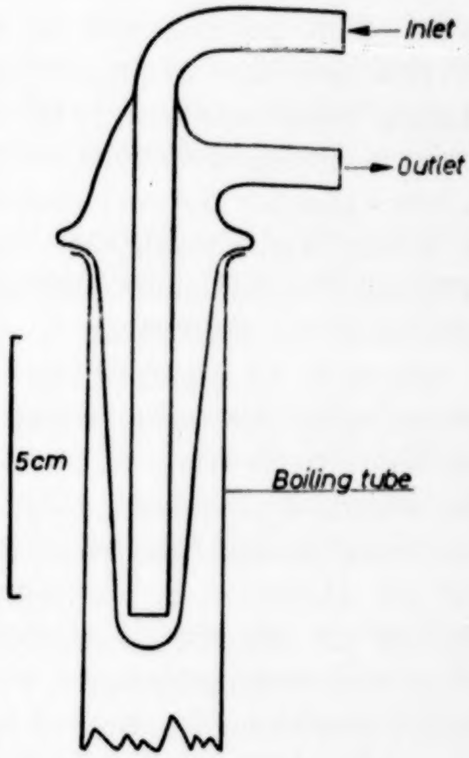

Fig. 1. "Cold finger" condenser.

DEVELOPMENT OF THE METHOD

Solutions of 5*M* calcium chloride having a pH of 1-2 and containing either copper, lead, chromium or nickel were prepared as outlined above and polarographed. The peak height due to each element was found to be proportional to its concentration in the range selected. This range corresponded to 5-50 p.p.m. of the element in the calcium metal.

Solutions of $5M$ calcium chloride having a pH of 6.5-7.5 and containing either lead, cadmium or manganese were also prepared and polarographed. Once again the peak height due to each element was proportional to concentration in the 5-50 p.p.m. range.

When all the elements were present together the waves due to copper, cadmium and manganese were free from interference, as was that due to lead in the solution of pH 6.5-7.5. In the pH 1-2 solution the nickel, chromium and lead waves were coincident.

Details of the method are given below.

METHOD

Solution of the sample

Add 50 g of the calcium metal sample, a little at a time, to 100 ml water in a 900 ml beaker. Cool periodically in an ice bath. From time to time add $10M$ hydrochloric acid to dissolve the calcium hydroxide formed. After addition of all the calcium add sufficient $10M$ hydrochloric acid to make the total volume used 250 ml.

Heat the solution to boiling and if any calcium hydroxide still remains, add 5 ml portions of $10M$ hydrochloric acid until it is completely dissolved. Add 0.5 ml 100 volume hydrogen peroxide and boil for 5 minutes. Allow the solution to stand overnight and filter through a Whatman No. 42 filter paper. Dry the filter paper and ash at bright red heat in a silica crucible until no trace of carbon remains. Transfer the residue to a boiling tube fitted with a "cold finger" condenser (Fig. 1). Add 2.0 ml $12M$ (fuming) perchloric acid and heat gently until all the residue is dissolved. Cool, dilute to 20 ml, boil for 2 minutes with 0.5 ml 100 volume hydrogen peroxide and add the main bulk of the solution.

Transfer the calcium solution to a 500 ml flask and make up to volume with water. Shake vigorously and, if necesssary, remake up to volume with water (Note 1).

Determination of copper and chromium

Pipette 20 ml of the calcium solution into a 50 ml tall-form beaker fitted with a coverglass. Evaporate slowly on a hot plate until a crust begins to form on the surface of the solution (Note 2). Allow to cool, rinse down the sides of the beaker and the coverglass with water and re-heat until the crust begins to form. Cool.

Add 2.0 ml $0.5M$ hydrochloric acid and re-heat until the contents are wholly liquid. Transfer the solution to a 10 ml graduated flask and make up to the mark with washings from the beaker. Shake the flask and remake up to volume, if necessary, with water (Note 1).

Deoxygenate a portion of the solution and polarograph, using the mercury pool as anode. Measure the height of the copper peak, obtained at about —0.35 volts on the cathode ray tube screen with the start potential set at —0.1 volts. Reset the start potential to —0.2 volts and measure the height of the peak due to chromium, nickel and lead, which occurs between —0.55 and —0.6 volts.

Determination of lead, cadmium and manganese

Pipette 20 ml of the calcium solution into a 50 ml tall-form beaker fitted with a cover glass. Evaporate slowly on a hot plate until a crust begins to form on the top of the solution (Note 2). Rinse down the sides of the beaker and the cover glass and re-heat until the crust again begins to form. Cool.

Add 2.0 ml water and re-heat until the contents are wholly liquid. Transfer to a 10 ml graduated flask and make up to the mark with washings from the beaker. Shake the flask and remake up to the mark, if necessary, with water (Note 1).

Transfer a 4.0 ml aliquot of the solution to a polarographic cell. Add 0.50 ml $0.1M$ sodium acetate solution, 0.25 ml $0.1M$ sodium hydroxide solution and 0.25 ml water. Deoxygenate the solution and, with the start potential set at —0.2 volts, measure the height of the peak due to lead on the cathode ray polarograph, which occurs at —0.55 volts (mercury pool).

Change the start potential to —0.5 volts and measure the height of the peak due to cadmium which occurs at —0.8 volts. Reset the start potential to —1.1 volts (Note 3) and measure the height of the peak due to manganese which occurs at —1.45 volts.

Calculation of results and calibration

The concentrations of the elements determined above may be obtained by the use of suitable calibration factors. Allowance must be made for the "reagent blank" which is determined as explained below.

Standard calcium chloride solution

Add 125 g pure calcium carbonate, a little at a time, to 250 ml $10M$ hydrochloric acid in a 1 litre tall-form beaker. Add 0.5 ml 100 volume hydrogen peroxide and boil for 5 minutes. Cool, transfer to a 500 ml graduated flask and make up to volume with water. Shake and, if necessary, remake up to the mark with water (Note 1).

Determination of the calibration blank

Pipette a 20 ml aliquot of the standard calcium solution into each of two 50 ml tall form beakers and carry out the determinations exactly as already described in the method.

Determination of the reagent blank

Transfer a 10 ml aliquot of the 10*M* hydrochloric acid used in the method to each of two 50 ml tall-form beakers provided with coverglasses. Evaporate just to dryness. Pipette a 20 ml aliquot of the standard calcium solution into each of the beakers and carry out the determination exactly as described in the method. Subtract the "calibration blank" peak heights from the peak heights thus obtained. This is the reagent blank which must be subtracted from the values obtained with the sample under test.

Evaluation of calibration factors

A. Prepare standard solutions of copper, chromium, nickel and lead (Note 4). Place four 20 ml aliquots of the standard calcium solution in 50 ml tall-form beakers and treat as follows:

1. Add aliquots of the standard copper and chromium solutions to the first beaker and carry out their determination as described in the method.
2. Add an aliquot of the standard nickel solution to the second beaker and carry out a determination exactly as described for chromium in the method.
3. Add an aliquot of the standard lead solution to the third beaker and again proceed as for the determination of chromium.
4. Add an aliquot of the standard lead solution to the fourth beaker and carry out the determination of lead as described in the method.

Use the values of peak heights obtained above to calculate peak-height concentration factors for the copper, chromium and lead determinations and the correction factor for nickel.

B. Prepare standard solutions of cadmium and manganese (Note 4).

Add aliquots of these standard cadmium and manganese solutions to a 20 ml aliquot of the standard calcium solution in a 50 ml tall-form beaker and determine these elements as described in the method.

Use the peak-height values obtained to calculate the peak-height concentration factors for cadmium and manganese.

Notes

1. There is a contraction in volume when very concentrated calcium chloride solutions are diluted and this often necessitates readjustment of volumes after shaking.
2. The crust begins to form on the calcium chloride solution when the volume has been reduced to about 5 ml.
3. When a start potential as great as —1.1 volts is employed it may be necessary to adjust the height of the mercury reservoir. This is in order to maintain a suitable drop-time at the dropping mercury electrode so that synchronisation of the cathode ray polarograph is retained.

4. The standard solutions should be prepared in chloride medium and should be of such concentration that, after treatment, their final concentration is within the range encountered in the samples.

DETERMINATION OF VERY LOW CONCENTRATIONS

In order to determine the ultimate sensitivity of the method it was decided to extend the range of the calibration of one of the impurities. Cadmium was chosen because it has very satisfactory polarographic characteristics and because the samples of calcium available had very low cadmium levels.

The calibration graphs obtained were linear down to a concentration of approximately $10^{-6}M$ cadmium, which corresponds to 0.5 p.p.m. in the calcium metal. Below this level interference began to be encountered and this was shown to be due to the presence of nickel, whose reduction wave at this concentration extends into that of the cadmium.

It was calculated that, even at pH 9, the amount of Ni^{+2} ions still remaining in solution would be comparable with the amount of cadmium being determined.

The cathode ray polarograph was by no means on its maximum sensitivity setting in this range and it was thus emphasised that the ultimate sensitivity of polarographic methods depends upon the availability of methods for very complete removal of interfering elements rather than upon the attainable instrumental sensitivity.

Some further experiments on the determination of cadmium were carried out using dimethylglyoxime to remove the traces of nickel. In this way determinations of cadmium present in concentrations considerably below 0.5 p.p.m. were successfully carried out. The technique was, however, found to be too complicated for routine work as the slightest excess of dimethylglyoxime had the effect of very seriously distorting the cadmium wave.

At the high sensitivities employed for this work the cadmium step was often ill defined. An extrapolation method of measurement was therefore adopted as shown in Fig. 2.

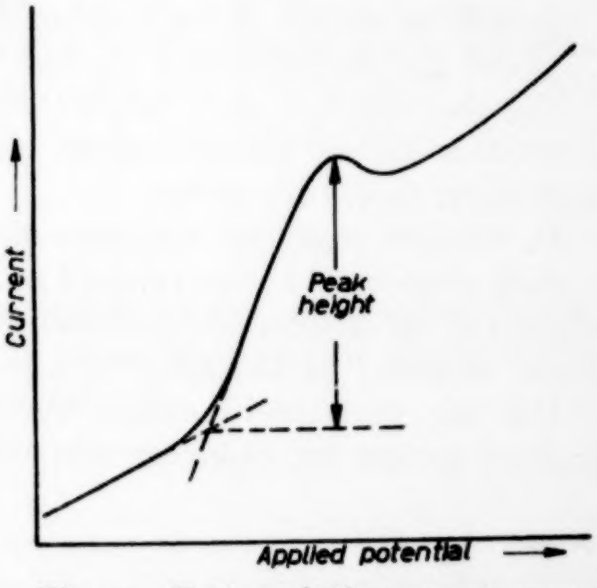

Fig. 2. Extrapolation measurement of the cadmium step.

TESTING OF THE METHOD

The method described above was tested by carrying out analyses of solutions prepared from a bulk sample of very pure calcium metal, to which various known

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amounts of impurities had been added at the dissolution stage. The nickel contents were determined by an absorptiometric procedure using dimethylglyoxime.

The results of these determinations are given in Table II. The figures quoted have been corrected for the amounts of each element initially present in the calcium metal and for that introduced in the reagents.

TABLE II

Sample	p.p.m. Nickel		p.p.m. Copper		p.p.m. Lead		p.p.m. Chromium		p.p.m. Cadmium		p.p.m. Manganese	
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
1	20	19.0	10	8.9	5	4.5	5	4.8	5	4.5	25	24.9
2	10	10.0	50	51.6	10	10.1	20	19.7	2	1.5	15	14.8
3	5	4.8	20	20.9	5	4.9	50	51.0	1	1.2	10	9.8
4	15	15.2	5	5.7	15	15.3	25	24.4	5	5.4	50	47.4
5	20	19.4	30	31.2	20	19.5	10	9.9	10	9.9	100	98.3

CONCLUSIONS

The investigations described in this and in previous papers have resulted in the development of a satisfactory polarographic method for the routine determination of trace amounts of copper, chromium, lead, cadmium and manganese in calcium metal. It has also been shown that concentrated calcium chloride is a very satisfactory base electrolyte, especially for the determination of very small amounts of reducible materials. As the level obtainable, however, is often less than the solubility product of interfering elements, improved methods of separating or complexing these interfering elements are needed to extend further the limits of detection.

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SUMMARY

The results of investigations discussed in this and previous papers are employed to develop a polarographic method for the determination of copper, chromium, lead, cadmium and manganese in calcium metal. Full details of the method are given and results and conclusions are presented.

RÉSUMÉ

Les résultats des recherches, donnés dans ce travail et dans des publications antérieures, sont utilisés pour le développement d'une méthode polarographique servant au dosage du cuivre, du chrome, du plomb, du cadmium et du manganèse dans le calcium métallique. Les détails de la méthode sont donnés, ainsi que les résultats et les conclusions.

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ZUSAMMENFASSUNG

Die Ergebnisse von in dieser und in früheren Arbeiten besprochenen Untersuchungen werden verwendet um eine polarographische Methode zur Bestimmung von Kupfer, Chrom, Blei, Cadmium und Mangan in metallischem Calcium zu entwickeln. Alle Einzelheiten der Methode werden gegeben und Ergebnisse und Schlüsse vorgelegt.

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THE REACTION OF CHROMATE WITH DIPHENYLCARBAZIDE. I

by

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The colour reaction between chromate and diphenylcarbazide in acid medium is the best method yet devised for the detection and colorimetric estimation of very small amounts of chromium. CAZENEUVE[1], the pioneer in this field, was of opinion that the intense coloration was due to an organo-metallic chromium compound. He obtained the compound in the form of a violet amorphous powder but its composition varied with the conditions of preparation. Later MOULIN[2] made a more systematic attempt at the isolation of the coloured compound but without any ultimate success. The soluble red-violet compound has not yet been isolated in the pure state and FEIGL[3] in his book on spot tests has simply mentioned that it is a soluble violet compound of unknown composition. Later he assumes that "a heteropolyacid may be formed between chromic acid and diphenyl carbazide[4]" and that the coloration is due to this polyacid. He admits, however, that experimental proof for such a formulation is lacking. BABKO AND PALIÎ[5] have very recently reported that the violet coloration when extracted with amyl alcohol from an aqueous solution, contains no chromium and they have attributed the colour to an ordinary oxidation product of carbazide without any complex formation. According to them, the action of chromate is a case of 'specific oxidation'. Such specificity in a simple oxidation reaction in the absence of complex formation is rather difficult to understand. BABKO's work, therefore, does not appear tomake any further headway in clarifying the mechanism of this classical reaction. Thus, the course of the chromate carbazide reaction is yet to be explained. The present work is an attempt to elucidate the mechanism of the reaction in solution from different physicochemical points of view.

A very striking feature of the chromate-carbazide reaction is that the chromium must be present in its hexavalent state and the reaction medium should be sufficiently acidic (0.2N is the optimum acidity). When the solution is alkaline, diphenylcarbazide does never react with chromate. This indicates that the reaction is primarily a redox one. However, since other oxidising agents like nitrate, permanganate, ceric salts, iodine, etc. fail to produce the characteristic violet colour with carbazide, it appears probable that the colour produced with chromate is due to some secondary complex formation. Oxidation, of course, plays a primary role in the complete process leading to colour formation.

Diphenylcarbazide when oxidised with chromate may give rise to carbazone or to its still higher oxidation product carbadiazone or the carbazide molecule itself may be completely ruptured at C=O linkage. The chromate molecule, on the other hand, will be simultaneously reduced during the oxidation process and chromium in a lower state of valence is expected, which may act as a cation in further complex formation. This is an important factor, since both carbazide and carbazone (but not carbadiazone) are known[6] to be typical agents which can combine with a large number of metal ions to produce intensely coloured inner complex salts. Reduction of chromate (Cr^{+6}) in acid medium leads generally to the tervalent Cr^{+3} stage. But chromic chromium is known to be non-reactive towards either carbazide or carbazone. The obvious conclusion is that Cr in the bivalent state (Cr^{+2}) is the ion responsible for the colour reaction. With these premonitions, the effect of chromous and chromate salts on carbazide and carbazone were studied separately to determine the causative agents really responsible for the colouration produced.

EXPERIMENTAL

Reagents and materials

The reagents used were either of 'AnalaR' grade or were prepared and purified in the laboratory. Fresh solutions of the reagents were always employed. The solutions of diphenylcarbazide and diphenylcarbazone were mixed separately with chromate and chromous salts in acid medium (0.2*N*). The results are given in Table I . In case of chromous solutions, it is preferable to work in absence of air though the reaction does take place to some extent even if air be not excluded.

TABLE I

Colour reaction of the different systems

(1)	Chromate + carbazide	same red violet coloration*
(2)	Chromate + carbazone	
(3)	Chromous + carbazone	
(4)	Chromous + carbazide	no coloration

*Excess of chromate in case of (1) and (2) and excess of chromous in case of (3) discharge the colour.

It will be found from the above table that Cr^{+2} in reaction (4) fails to produce any coloration, whereas all the other three reactions give rise to similar red violet colour. Though colour itself has long been considered as being characteristic of a definite molecular species, it is prudent not to rely on visual observations alone. So the recognised method of comparing the characteristic absorption spectra was applied for the identification of the compound responsible for the red-violet colour produced in all the three reactions (1), (2) and (3) already mentioned. The optical measurements of these systems were performed with a Beckman Quartz Spectrophotometer Model DU using 1-cm corex cells. The tungsten lamp was employed as the light source. The results are shown in Fig. (1).

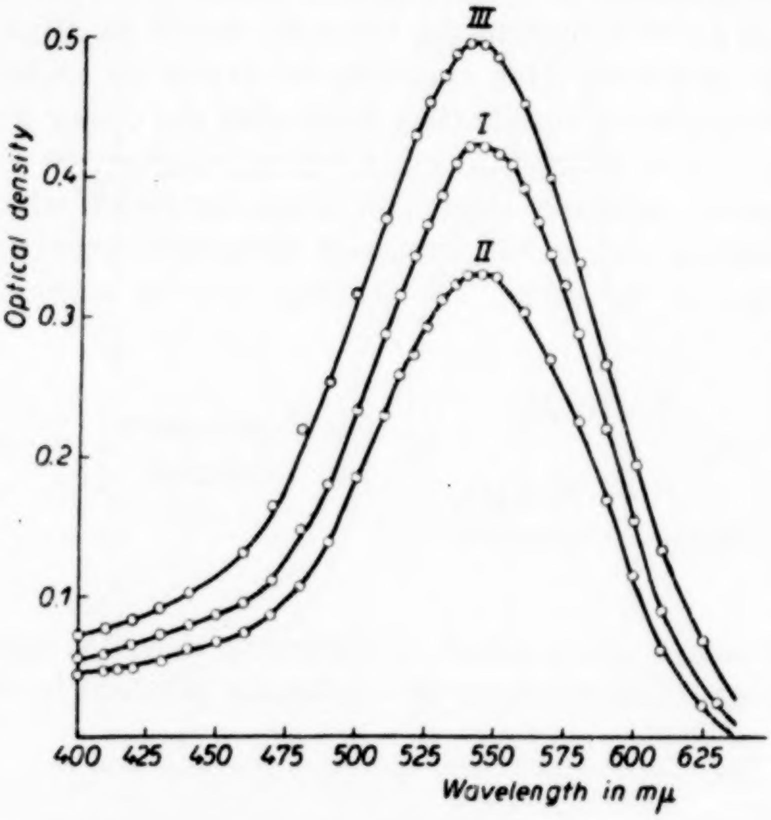

Fig. 1. Absorption spectra of three different systems
I — Chromate-carbazide
II — Chromate-carbazone
III — Chromous-carbazone

DISCUSSION

All the curves are found to be of similar nature and show a maximum absorption at 540 mμ. The spectral results thus indicate that the coloured reaction products in the three systems are identical. It seems probable, therefore, that the oxidation of carbazide by chromate produces carbazone which reacts with the Cr^{+2} produced by the reduction of chromate itself giving the characteristic colour. In case of the chromate-carbazone system, it is reasonable to assume that the chromate oxidises carbazone to its higher oxidation product and the chromous

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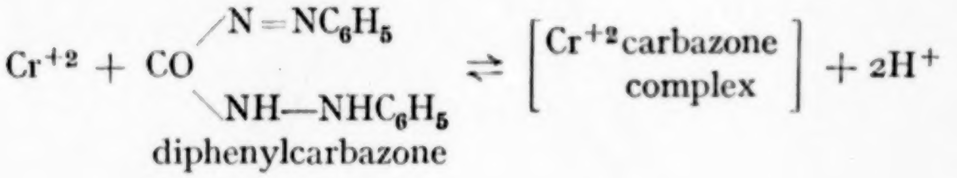
ion, thus formed, reacts with excess of carbazone present in the medium. Thus, both carbazone and carbazide may be employed for the reaction with chromate. Carbazide, however, seems to be more sensitive than carbazone as has also been observed by KRUMHOLZ[7]. But that carbazone is the organic molecule involved in the colour formation is borne out from the fact that it is the only common constituent present or produced as a result of reaction in the 3 different systems. In system (3) the formation of carbazide by the reduction of carbazone molecule with Cr^{+2} ions may be visualised but the independent action of Cr^{+2} ion on carbazide (free from carbazone) in system (4) disproves such a formulation. On the contrary, excess of Cr^{+2} in system (3) has been found to cause the discharge of colour initially produced. This can only be explained as being due to the reduction of carbazone to carbazide thus destroying the colour forming capacity. Moreover, reaction (2) cannot by any stretch of imagination be considered to produce the carbazide molecule. Hence, the only conclusion which seems logical is that the components responsible for colour formation is carbazone on the one hand and Cr^{+2} ions on the other. The reaction may be expressed as



$$Cr^{+2} + CO\begin{matrix} \diagup N{=}NC_6H_5 \\ \diagdown NH{-}NHC_6H_5 \end{matrix} \rightleftarrows \left[\begin{matrix} Cr^{+2}\text{carbazone} \\ \text{complex} \end{matrix}\right] + 2H^+$$

The discharge of colour when excess of chromate is added may be explained as due to the complete oxidation of the carbazone involved in the combination.

PRESENCE OF A SINGLE COLOURED COMPLEX

The reaction systems (1), (2) and (3) have been shown to contain the same coloured complex. It is still necessary to establish unequivocally that the reaction product is a single coloured complex. This is done by the method of VOSBURGH AND COOPER[8] who showed that, in the case of a mixture of several coloured complexes, the absorption spectra of solutions containing the reactants in different molar proportions in which they were expected to react, would not show a constant wavelength of maximum absorption. In the present case, therefore, mixtures of chromate-carbazide solutions were prepared in the molar ratios of 1:1, 1:2 and 1:3 keeping the chromium concentration constant and the spectral curves were determined with a Lumetron Photoelectric Colorimeter Model 402 EF. The results are indicated in Fig. 2. In all the cases, the wavelength of maximum absorption remains unchanged, thereby excluding the possibility of formation of several complexes.

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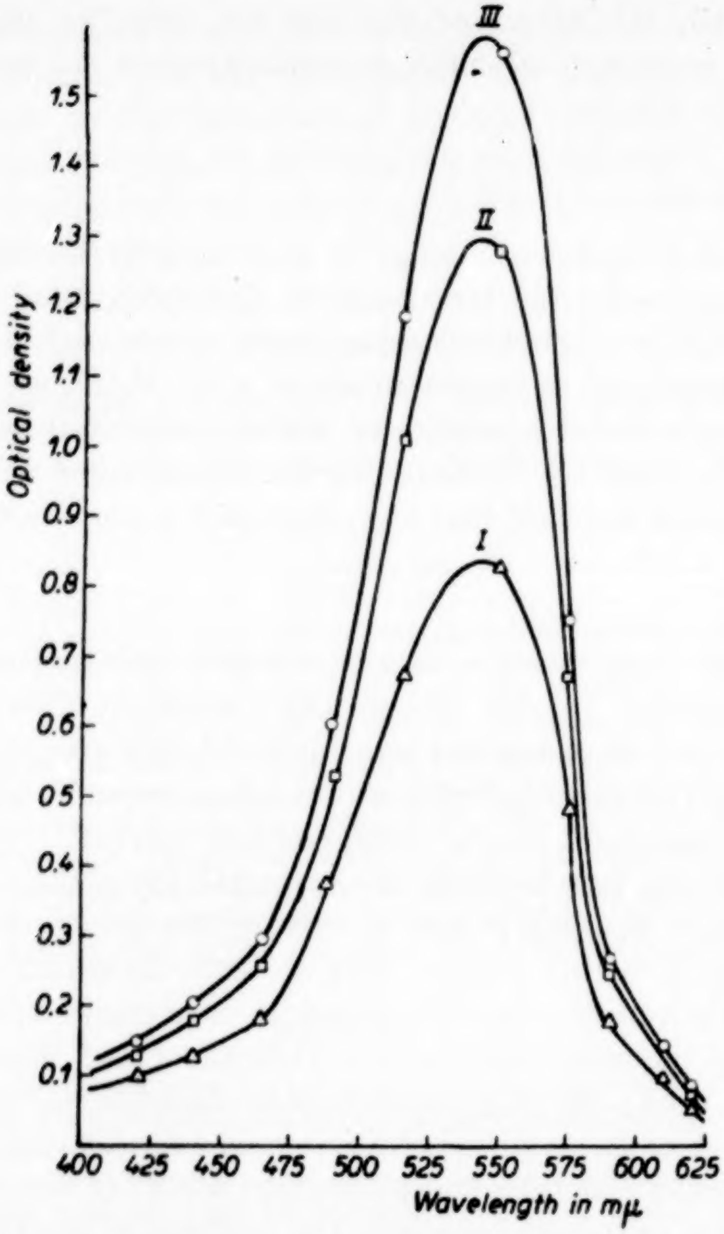

Fig. 2. Absorption spectra of chromate-carbazide mixtures containing the reactants in different molar proportions (Cr^{+6} concentration remaining constant $= 2 \cdot 10^{-5} M$)

I — Cr^{+6} : carbazide = 1 : 1
II — Cr^{+6} : carbazide = 1 : 2
III — Cr^{+6} : carbazide = 1 : 3

NATURE OF THE COMPLEX FORMED

CAZENEUVE's original idea that the coloured reaction product is an organometallic chromium complex thus seems to be vindicated. Nevertheless, the above studies are rather insufficient to throw any light on the exact nature of the complex formed. The coloured Cr^{+2}-complex may either be a monovalent cation or an inner complex salt. The alternative formulations, however, envisage a great divergence in the properties of the complex and hence with a view to decide, once for all, the nature of the complex, whether electrolytic or not, migration studies as well as solubility determinations in non-polar solvents were carried out.

Transport experiments

The apparatus employed was similar to that used by DUVAL[9]. Since concentrated solutions are preferable for transport determinations, almost saturated solutions of carbazide in alcohol was mixed with aqueous acidified chromate and this mixture was subjected to migration study. 0.1*N* H_2SO_4 was employed as the indifferent electrolyte for the passage of electric current through the solution. Even after 4 hours of electric current, the red colour failed to move within the limbs of the apparatus showing that the compound is non-electrolytic in nature.

Solubility studies

The solubility of a compound in various non-polar solvents usually indicates its inner complex nature[10]. In the present case, solubility determination of the compound in the solid state was not possible and hence extraction from aqueous solution by various non-polar solvents was taken recourse to for ascertaining the solubility of the compound in the corresponding solvent.

CAZENEUVE[1] was the first to study the extractability of the compound. According to him, though benzene failed to extract the coloured compound, amyl alcohol was successful in this respect. Very recently, BERNHARDT *et al.*[11], in their attempt to estimate minute traces of chromium in uranium, succeeded in extracting the compound quantitatively with cyclohexanol and *n*-hexanol.

In the present work, the reagent carbazide dissolved in different non-polar solvents was added to an acidified chromic acid solution and the mixture was shaken in a stoppered test tube and allowed to settle. It was rather peculiar to find that the nature of the acid employed to acidify the reaction mixture had a profound effect on the partition of the coloured product between the 2 phases. In organic acid (AcOH) medium and with solvents C_6H_6 and $CHCl_3$ the coloured product was found to distribute itself between the 2 phases, the distribution being greatly in favour of the organic solvent, and with cyclohexanol, the aqueous layer was completely colourless. However, when mineral acids such as sulphuric acid was used the organic layer was almost colourless except in the case of cyclohexanol. Even then, the colour in the cyclohexanol layer is very much less in contrast to that produced in organic acid medium.

CONCLUSION

The transport experiment unequivocally proves that the coloured compound is non-electrolytic in character. The solubility in non-polar solvents is also indi-

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cative of its inner-complex nature. Moreover, the production of the intense colour by the action of chromate or chromous ion on the respective reagents may also be regarded as due to the formation of an inner-complex compound[12].

Thus, the reaction of carbazide or carbazone with chromium may be considered to be in conformity with their well-known property of forming inner-complex salts with other bivalent metals.

ACKNOWLEDGEMENT

The author's thanks are due to Prof P. B. Sarkar, Head of the Department of Chemistry for his keen interest and for providing laboratory facilities. Thanks are also due to Dr. B. C. HALDAR, lately of this department, for his helpful suggestions.

SUMMARY

The mechanism of the classical colour reaction between chromate and carbazide has been studied in solution from various physicochemical points of view. It has been established from spectral identity that the same red-violet compound is produced in the 3 different reaction systems, chromate-carbazide, chromate-carbazone and chromous-carbazone. This leads to the conclusion that the chromate-carbazide reaction is a composite one involving preliminary oxidation followed subsequently by complex formation. Moreover, the actual constituents involved in the reaction have been identified as Cr^{+2} on the one hand and carbazone on the other, giving rise to an intensely coloured inner complex compound. The inner complex nature of the coloured product was gauged independently from migration studies and from extraction of the coloured compound by non-polar solvents.

RÉSUMÉ

Le mécanisme de la réaction de coloration classique, entre un chromate et une carbazide, a été étudié par différents procédés physico-chimiques. Il a été démontré que le même composé rouge violet est formé dans les 3 réactions: chromate-carbazide, chromate-carbazone et chrome(II)-carbazone. Ceci permet de conclure que la réaction chromate-carbazide consiste d'abord en une oxydation suivie de la formation du complexe. D'autre part, le complexe obtenu par cette réaction est formé de Cr^{+2} et de carbazone, c'est un complexe interne fortement coloré. La nature de complexe interne du produit formé a été établie indépendamment par des études de migration et par extraction du composé coloré par des solvants non polaires.

ZUSAMMENFASSUNG

Der Mechanismus der klassischen Farbreaktion zwischen Chromat und Carbazid in Lösungen wurde von verschiedenen physikalisch-chemischen Gesichtspunkten aus untersucht. Durch die spektrale Identität wurde festgestellt, dass die gleiche rotviolette Verbindung in drei verschiedenen Reaktionssystemen (Chromat-Carbazid, Chromat-Carbazon und Chrom-II-Carbazon) entsteht. Dies führte zu dem Schluss, dass die Chromat-Carbazid-Reaktion zusammengesetzt ist aus einer zuerst erfolgenden Oxydation mit nachfolgender Komplexbildung. Darüber hinaus wurden die tatsächlich an der Reaktion beteiligten Bestandteile einerseits als Cr^{+2} und anderer seits als Carbazon identifiziert, die zusammen den intensiv gefärbten inneren Komplex entstehen lassen. Die innere Komplexnatur des gefärbten Produktes wurde unabhängig von einander aus Wanderungsuntersuchungen und durch Extraktion der gefärbten Verbindung mit nichtpolaren Lösungsmitteln gemessen.

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THE REACTION OF CHROMATE WITH DIPHENYLCARBAZIDE. II

by

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In our previous communication[1], the individual constituents responsible for the colour formation in the chromate-carbazide reaction were indicated. The present work discusses the stoichiometry of the reactions

chromate + diphenylcarbazide . . . . (1)
chromate + diphenylcarbazone . . . . (2)
chromous + diphenylcarbazone . . . . (3)

which is very vital for the complete elucidation of the various steps leading to colour formation. The stoichiometry of any chemical reaction presupposes a general idea of the reactants and products formed in the course of the reaction. Thus, only on the basis of a thorough knowledge of the composition of the coloured complex formed, it is possible to formulate the complete stoichiometric relation of the aforesaid reactions. Amongst the methods available for the investigation of coloured complexes in solution[2], it appeared that JOB's[3] method of continuous variation for the independent determination of the composition of the complex, would be particularly suitable in this case. The utility of JOB's method will be appreciated when one considers the various complexities in the different reaction systems, particularly in (1) and (2), which renders the other methods involving a simultaneous determination of the formula and stability of the complex, not very suitable for the purpose.

EXPERIMENTAL

The experimental study of the different reaction systems may be subdivided broadly into two categories

a) studies in equimolecular solutions for the composition of the complex formed,

b) studies in non-equimolecular solutions for finding out the equilibrium constants (K).

Apparatus

All the transmittancy measurements were made with a Lumetron Photoelectric

Colorimeter Model 402EF of Photovolt Corporation employing a cell of thickness 20 mm and capacity 16 ml.

Reagents and Materials

The reagents employed were either of 'Analar' grade or were prepared and purified in the laboratory.

K_2CrO_4 solutions were prepared from Merck's pro analysi K_2CrO_4 and were standardised volumetrically.

Standard solution of diphenylcarbazide was prepared by direct weighing of perfectly white Merck's pro analysi reagent and dissolving it in a minimum amount of alcohol and finally diluting with freshly boiled water. Solutions were prepared immediately before mixing as otherwise oxidation occurred.

Diphenylcarbazone was prepared by the oxidation of carbazide according to the method of SLOTTA AND JACOBI[4] and the crude product, thus obtained, was purified by repeated crystallisation from 75% alcohol till it melted at 157°. Standard solutions were prepared as in the case of carbazide. In presence of sunlight the colour of the solution usually fades away indicating instability of the compound in solution.

Standard $0.4N$ H_2SO_4 was prepared from E. Merck's G. R. quality acid.

Chromous sulphate solutions were prepared according to ZINTL AND RIENÄCKER's[5] method starting from $CrCl_3.6H_2O$ and purifying the chromous salt through the insoluble acetate. The chromous sulphate solution was stored in hydrogen atmosphere. The purity of the reagents were rather important in ensuring the stability of the chromous solutions. The chromous solution was standardised potentiometrically[6] before each experiment.

Preparation of reaction mixtures for studies in equimolecular and non-equimolecular solutions

The reagents, the procedure and the precautions are the same in both the cases, only the concentrations of the reactants in the mixture dealt with, are equal in one case, while they are not in the other.

Throughout the work, the acidity of the medium in the systems (1), (2) and (3) was maintained at $0.2N$. Since the colour reaction is extremely sensitive, the solutions employed for the study of the maximum composition were made very dilute (0.0001 M or less). In preparing mixtures, it is rather important to add the chromium salt to the reagent solutions and never the reverse, as otherwise the reagents may be destroyed by localised action. Reaction mixtures were prepared by adding the two components in varying proportions. In case of (3) the addition of chromous salt has to be performed in absence of air. For this purpose, the acidified carbazone solution was first freed from air by bubbling oxygen-free N_2 (passed through $CrCl_2$ solutions) through it and then the addition of the chromous sulphate and subsequent colour development was completed in the current of N_2.

The reactions were carried out in perfectly cleansed Jena or Pyrex vessels and throughout the work conductivity water was used. In all the 3 systems, the colour of the solutions remains stable for several hours. Nevertheless, the transmission measurements should preferably be taken soon after mixing.

Chromate-carbazide system

In this case, the reagent carbazide is colourless and though K_2CrO_4 solutions are coloured, at the dilutions employed, they are for all practical purposes colourless. Hence, for determining the maximum composition the observed optical densities (O.D's) are directly plotted against composition (x). The transmittancy measurements were done at two wavelengths as suggested by VOSBURGH[6] to corroborate the presence of a single coloured complex mentioned previously[1]. The results are indicated in Figs. (1) and (2).

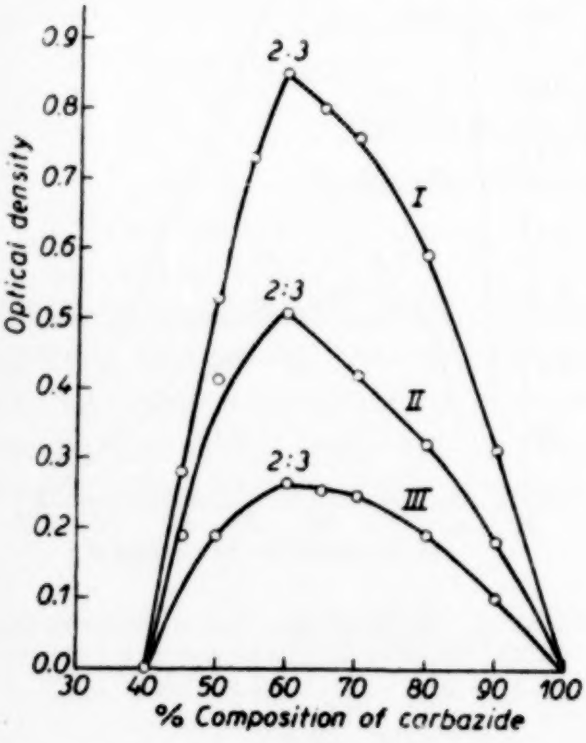

Fig. 1. Optical density of equimolecular chromate-carbazide mixtures at 550 mμ (I) 4.10^{-5}M; (II) 3.10^{-5}M; (III) 2.10^{-5}M

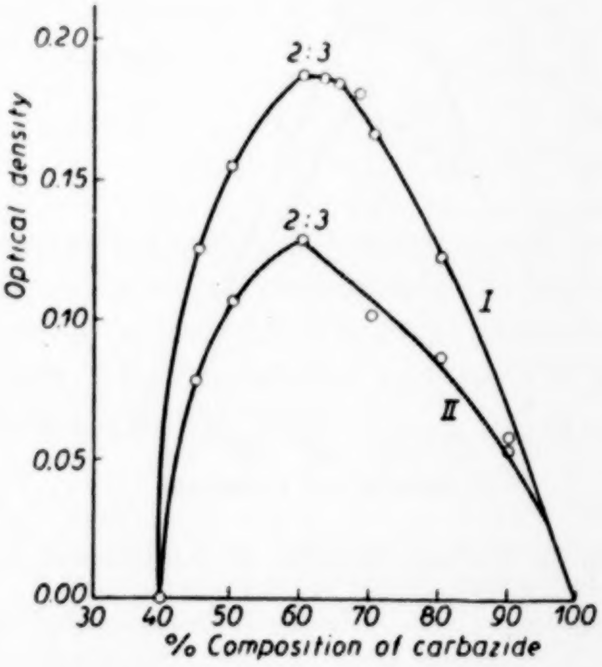

Fig. 2. Optical density of equimolecular chromate-carbazide mixtures at 465 mμ (I) 4.10^{-5}M; (II) 3.10^{-5}M

It is apparent from the curves that the maximum composition corresponds to a chromate: carbazide ratio equal to 2:3. The maximum composition is the same for different initial concentrations of the equimolecular mixtures. As expected, the maximum is found to be independent of the wavelength of light, thus confirming the existence of a single complex in the system.

Chromate-carbazone system

Here the reagent carbazone is coloured but preliminary experiments indicated that at 550 mμ and at the dilutions employed, its contribution to the optical density values could be neglected and hence the observed O.D. values were directly plotted against composition (x). The results shown in Fig. (3) indicate the same maximum composition at chromate:carbazone ratio equal to 1:3 for the different initial concentrations of the equimolecular mixtures.

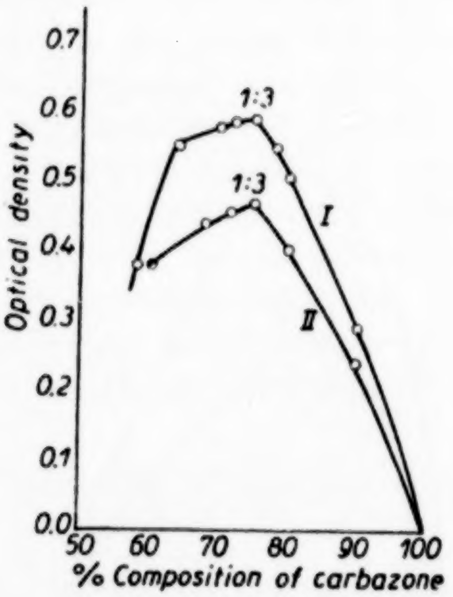

Fig. 3. Optical density of equimolecular chromate-carbazone mixtures at 550 mμ (I) $8.10^{-5}M$; (II) $4.10^{-5}M$

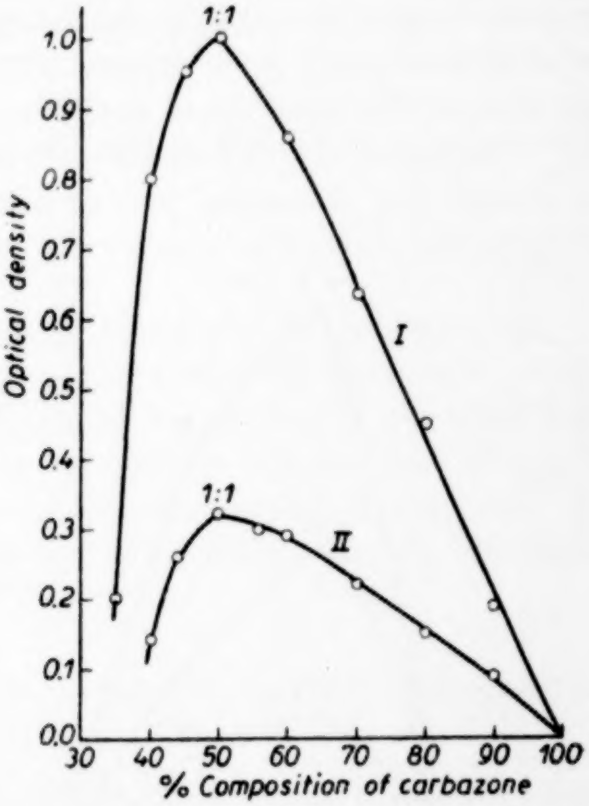

Fig. 4. Optical density of equimolecular chromous-carbazone mixtures at 550 mμ (I) $1.25.10^{-4}M$ (II) $5.10^{-5}M$

Chromous-carbazone system

The O.D. values of the blank acidified carbazone-water mixtures were first determined. These values were subtracted from the observed O.D. values of the mixture. The corrected O.D.'s were then plotted against composition of the solution as shown in Fig. 4. The maximum composition in this case was found to correspond to the chromous-carbazone ratio equal to 1:1 and as in previous cases it is independent of the concentration.

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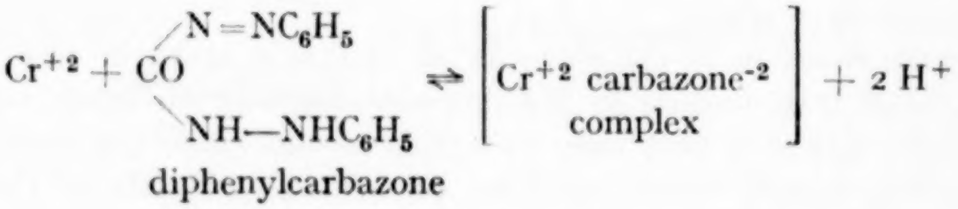
DISCUSSION

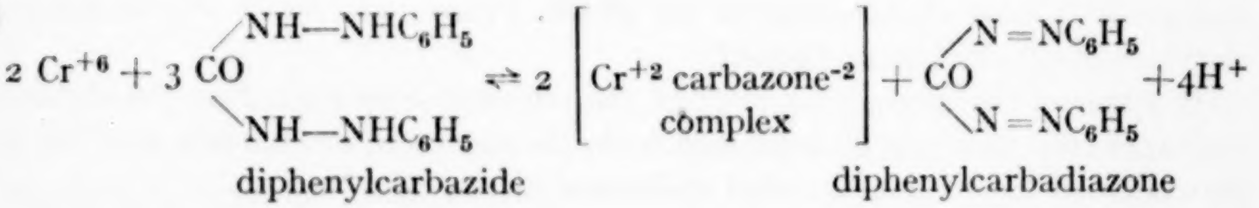
The maximum composition in equimolecular solutions is found to be 2:3 for system (1), 1:3 for system (2) and 1:1 for system (3) respectively. It can be seen, however, that of the three different reactions (1) and (2) are rather complex (in as much as they involve preliminary oxidation coupled with subsequent complex formation) and as such the maximum composition in these cases does not directly lead to an unequivocal formulation of either the composition of the complex or the stoichiometry of the corresponding reaction. Reaction (3), however, appears to be a simple case of displacement leading to colour formation and hence the maximum composition in this case can justifiably be considered as giving the proportion in which the constituents combine to form the coloured complex. Thus, from the experimentally observed maximum at 1:1, reaction (3) may be formulated as follows:



$$Cr^{+2} + \underset{\text{diphenylcarbazone}}{CO\begin{matrix}\diagup N{=}NC_6H_5\\ \diagdown NH{-}NHC_6H_5\end{matrix}} \rightleftharpoons \left[\begin{matrix}Cr^{+2}\text{ carbazone}^{-2}\\ \text{complex}\end{matrix}\right] + 2\,H^+$$

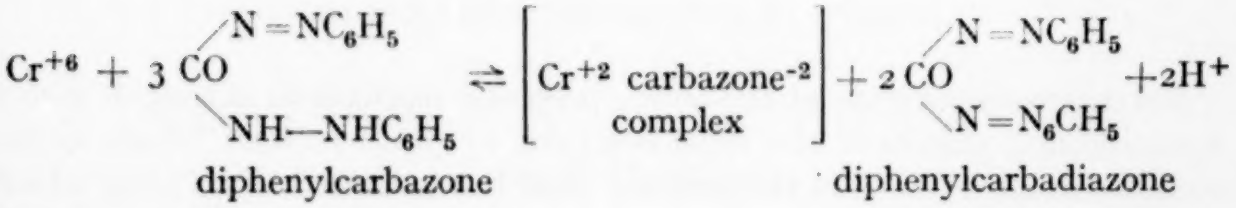
taking into account the inner complex nature of the coloured compound as shown earlier[1]. Proceeding from this formulation, we may try to correlate the values of maximum composition in case of reactions (1) and (2). The only consistent mechanism which embraces all the different reaction systems and appears to explain the experimentally observed facts is suggested below.

(1)



$$2\,Cr^{+6} + 3\,\underset{\text{diphenylcarbazide}}{CO\begin{matrix}\diagup NH{-}NHC_6H_5\\ \diagdown NH{-}NHC_6H_5\end{matrix}} \rightleftharpoons 2\left[\begin{matrix}Cr^{+2}\text{ carbazone}^{-2}\\ \text{complex}\end{matrix}\right] + \underset{\text{diphenylcarbadiazone}}{CO\begin{matrix}\diagup N{=}NC_6H_5\\ \diagdown N{=}NC_6H_5\end{matrix}} + 4H^+$$

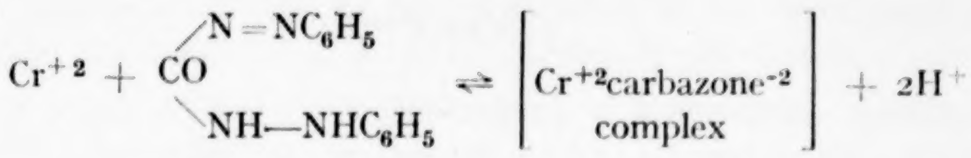
(2)



$$Cr^{+6} + 3\,\underset{\text{diphenylcarbazone}}{CO\begin{matrix}\diagup N{=}NC_6H_5\\ \diagdown NH{-}NHC_6H_5\end{matrix}} \rightleftharpoons \left[\begin{matrix}Cr^{+2}\text{ carbazone}^{-2}\\ \text{complex}\end{matrix}\right] + 2\,\underset{\text{diphenylcarbadiazone}}{CO\begin{matrix}\diagup N{=}NC_6H_5\\ \diagdown N{=}N_6CH_5\end{matrix}} + 2H^+$$

References p. 221.

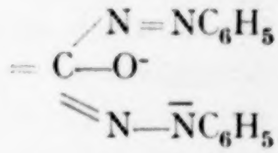
(3)



$$Cr^{+2} + CO\begin{matrix}\diagup N=NC_6H_5\\ \diagdown NH-NHC_6H_5\end{matrix} \rightleftharpoons \left[\begin{matrix}Cr^{+2}\text{carbazone}^{-2}\\ \text{complex}\end{matrix}\right] + 2H^+$$

diphenylcarbazone

where carbazone^{-2} =



$$C\begin{matrix}\diagup N=NC_6H_5\\ -O^-\\ \diagdown\!\!\diagdown N-\bar{N}C_6H_5\end{matrix}$$

The above proposed mechanism, while taking into account the fact that the same coloured complex is produced in all the 3 cases, explains satisfactorily the role of the two reagents carbazide and carbazone in the colour-forming reaction. Specially, the greater sensitivity of diphenylcarbazide as compared to carbazone for hexavalent chromium receives an adequate explanation. The determination of maximum compositions reveals that for the same chromate concentration, the amount of carbazone required is double that of carbazide and hence the superiority of the latter reagent.

The primary function of chromate as an oxidising agent in case of (1) and (2) is also taken into account in the proposed mechanism. Oxidation, however, is undoubtedly stepwise, first from carbazide to carbazone and then from carbazone to carbadiazone which has been considered to be one of the products of reaction in case of (1) and (2).

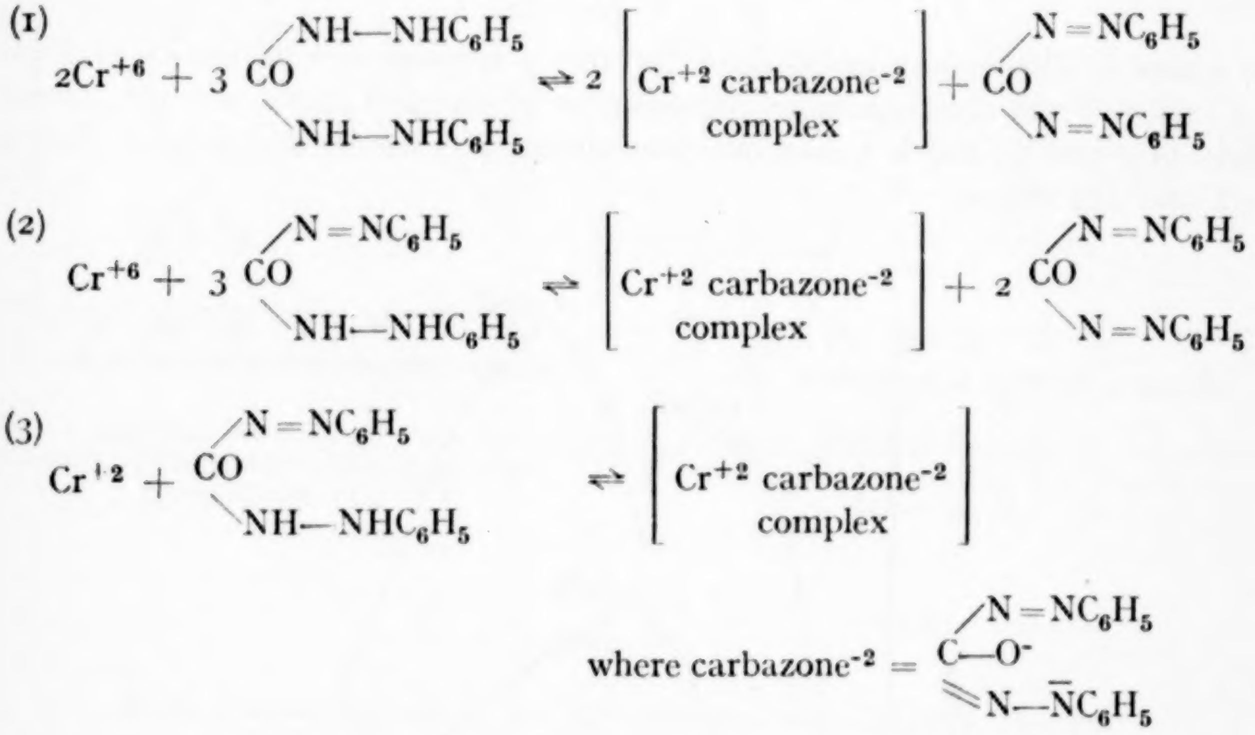
This mechanism also explains another feature in the composition-O.D. curves for the 3 different reaction systems, where, after the maximum composition mark, a small increase in the proportion of chromium shows a rapid diminution in O.D. and for a particular ratio of the reactants the colour vanishes. From reactions (1) and (2), it seems that after the maximum composition, any excess of chromate will oxidise Cr^{+2} to Cr^{+3} and the carbazone to carbadiazone or its higher oxidation product. In reaction (3), on the other hand, excess Cr^{+2} under similar conditions will simply reduce the carbazone to the carbazide which has been shown to be non-reactive towards bivalent Cr. In all the 3 cases, the result will be the rapid destruction of the colour formed.

It appears, therefore, that most of the relevant facts regarding the chromate-carbazide reaction can be explained from the aforesaid mechanism and this may be regarded as a valuable point in favour of the proposition.

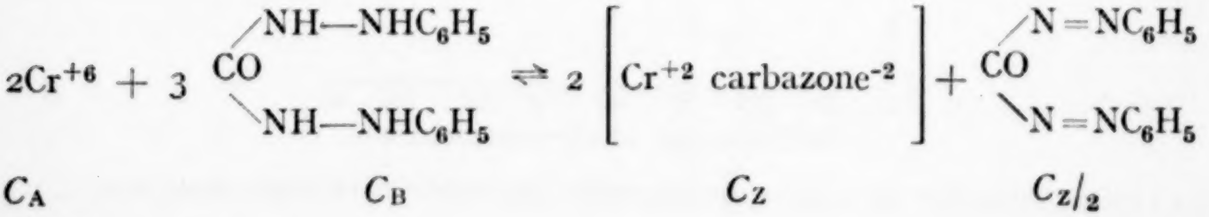
STUDIES IN NON-EQUIMOLECULAR SOLUTIONS

Further corroboration of the above proposed mechanism is sought from non-equimolecular studies of the three reactions by JOB's method which gives the equilibrium constant K of the systems. JOB[3] has indicated that in case of a reaction system where the maximum composition can be explained in more than one way, the constancy of the equilibrium constant (K) values calculated from the respective equations may be used as a criterion for distinguishing between the different possibilities. In the present work, studies in non-equimolecular solutions in case of reaction (3) will give the apparent dissociation constant of the complex and if this value is found to be reasonably constant, the simple displacement reaction stands vindicated. Further, if the K values in case of (1) and (2) give concordant results in each case, it may be safely asserted that the proposed mechanism is possibly the most appropriate formulation.

Since the 3 reactions are carried out in a strongly acid medium ($0.2N$), the quantity of acid liberated as a result of reaction (the solutions are extremely dilute $0.0001M$ or less) can be neglected in comparison with the acidity of the medium. Hence the reactions (1), (2) and (3) may for all practical purposes be rewritten in the following form.


(1)
2Cr+6 + 3 CO NH—NHC6H5 NH—NHC6H5 ⇌ 2 [Cr+2 carbazone-2 complex] + CO N=NC6H5 N=NC6H5
(2)
Cr+6 + 3 CO N=NC6H5 NH—NHC6H5 ⇌ [Cr+2 carbazone-2 complex] + 2 CO N=NC6H5 N=NC6H5
(3)
Cr+2 + CO N=NC6H5 NH—NHC6H5 ⇌ [Cr+2 carbazone-2 complex]
where carbazone-2 = C—O- N=NC6H5 N—N̄C6H5

These equations will henceforth be considered for the purpose of investigating the nature of the equilibria. Thus, K may be calculated in reaction (1) as follows:


2Cr+6 + 3 CO NH—NHC6H5 NH—NHC6H5 ⇌ 2 [Cr+2 carbazone-2] + CO N=NC6H5 N=NC6H5
CA
CB
CZ
CZ/2

Let the equilibrium concentrations of chromate, carbazide and the complex be C_A,C_B and C_Z respectively, whence carbadiazone concentration is $C_Z/_2$

$$\text{the equilibrium constant } K = \frac{C_A{}^2 \cdot C_B{}^3}{C_Z{}^2 \cdot C_Z/_2}$$

On performing the usual mathematical operation, one obtains K in terms of the initial concentration C, p and x, where p = ratio of the respective concentrations and x = the composition-maximum.

$$\text{Here } K = \frac{3}{4}\,\frac{C^2[x(2p+3) - 3]^5}{(3 - 5x)^3(p - 1)^2}$$

Similarly, for the chromate-carbazone system (2) and the chromous-carbazone system (3), the equilibrium constant K is given by

$$K = \frac{9}{4}\,\frac{C\ [3 - x\ (p+3)]^4}{(p - 1)\ (3 - 4x)^3}$$

and

$$K = \frac{C[x(p + 1) - 1]^2}{(p - 1)\ (1 - 2x)}$$

respectively. The experimental data for the 3 systems are indicated in Figs. 5, 6 and 7. From the maximum composition (x) in each curve and the known values of p and C, the K values are determined. The results are given in Tables I, II and III below.

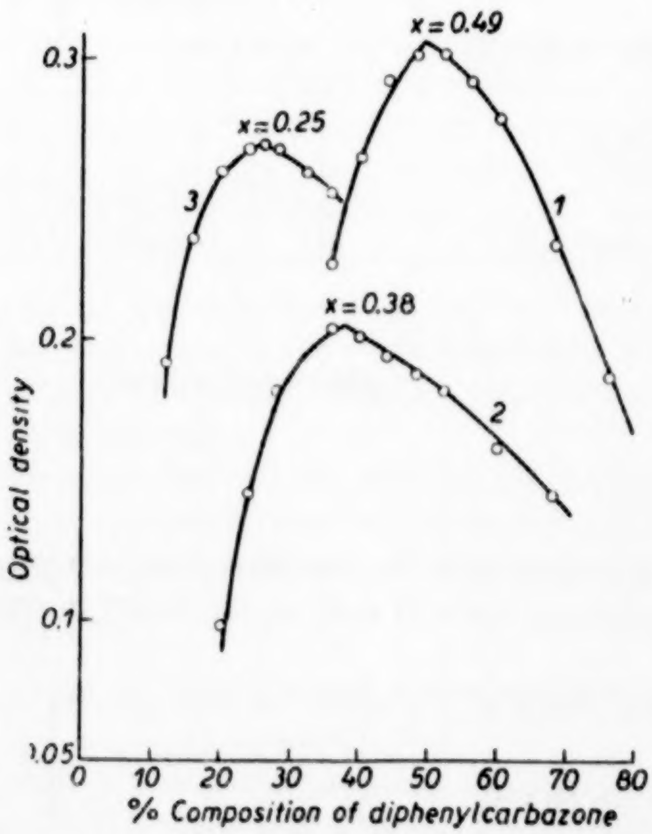


Fig. 5. Optical density of non-equimolecular chromate-carbazide mixtures

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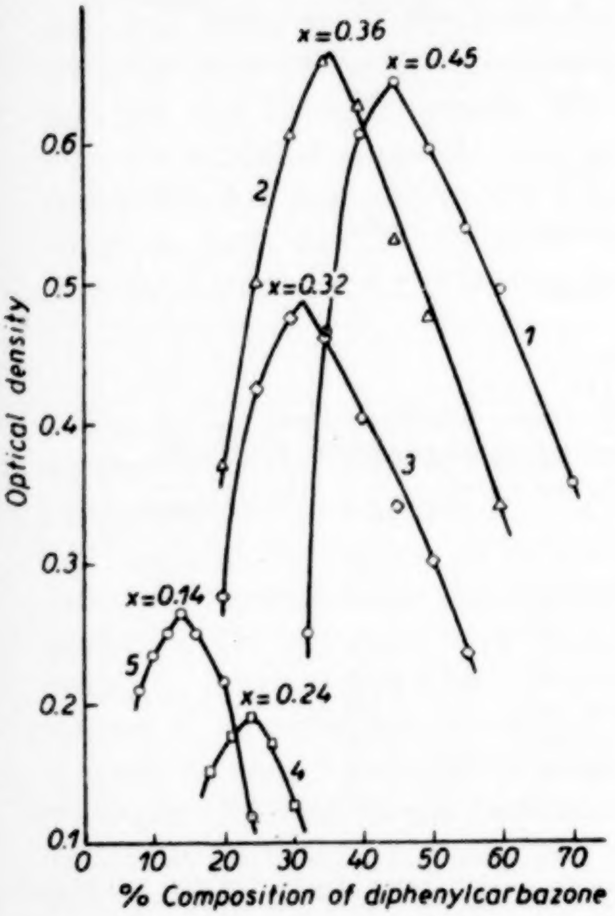

Fig. 6. Optical density of non-equimolecular chromate-carbazone mixtures at 550 mμ

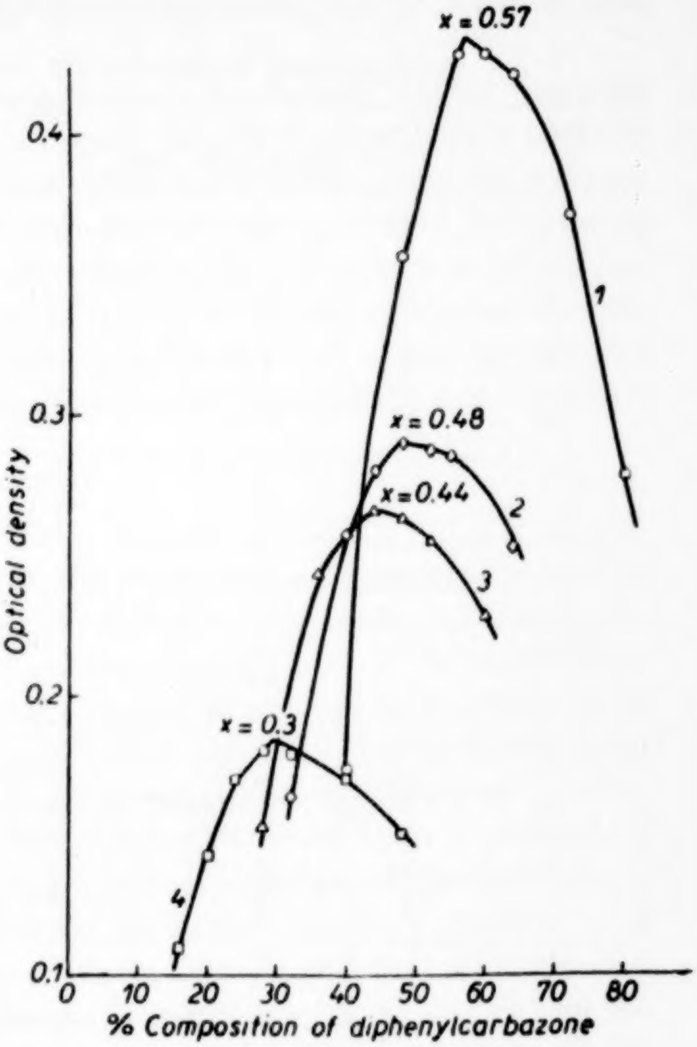

Fig. 7. Optical density of non-equimolecular chromous-carbazone mixtures at 550 mμ

TABLE I

EQUILIBRIUM CONSTANT OF THE CHROMATE-CARBAZIDE SYSTEM

Fig.	Curve	Conc. of chromate $(c) \times 10^{-6} M$	p	x	$K \cdot 10^{-12}$	Mean K
5	1	10	2	0.49	6.6	
5	2	5	4	0.38	3.6	$5.7 \cdot 10^{-12}$
5	3	5	10	0.25	6.8	

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TABLE II

EQUILIBRIUM CONSTANT OF THE CHROMATE-CARBAZONE SYSTEM

Fig.	Curve	Conc. of chromate (M)	p	x	$K\cdot 10^{-7}$	Mean K
6	1	$4\cdot 10^{-5}$	2	0.57	1.22	$2.3\cdot 10^{-7}$
6	2	$2\cdot 10^{-5}$	4	0.48	2.00	
6	3	$1.6\cdot 10^{-5}$	5	0.44	3.62	
6	4	$8\cdot 10^{-6}$	10	0.30	2.25	

TABLE III

DISSOCIATION CONSTANT OF THE CHROMOUS-CARBAZONE COMPLEX

Fig.	Curve	Conc. of $CrSO_4$ (M)	p	x	$K\cdot 10^{-6}$	Mean K
7	1	$2\cdot 10^{-4}$	1.25	0.45	1.25	$2.7\cdot 10^{-6}$
7	2	$1.25\cdot 10^{-4}$	2	0.36	2.85	
7	3	$1\cdot 10^{-4}$	2.5	0.32	2.69	
7	4	$5\cdot 10^{-5}$	5	0.24	4.65	
7	5	$5\cdot 10^{-5}$	10	0.14	2.25	

The value of K in reaction (3) gives only the apparent dissociation constant at a particular acid concentration. The true dissociation constant may be very different as acidity of the medium profoundly influences the dissociation of an inner complex salt.

CONCLUSION

The very great sensitivity of the reagents, the complete exclusion of air in (3), as well as the high dilutions at which the operations were carried out involved considerable error. Considering these limitations it may be said that the K values obtained are reasonably constant for the systems (1), (2) and (3), thus corroborating the mechanism proposed by the author.

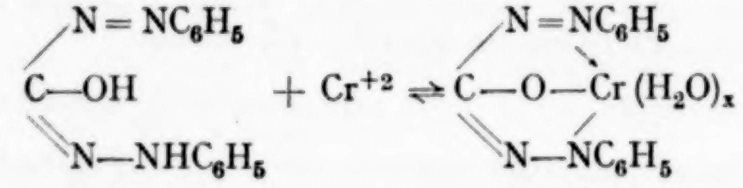
MAGNETOCHEMICAL MEASUREMENTS

The presence of bivalent chromium in the coloured complex has also been independently corroborated from magnetochemical measurements. The valence state of any paramagnetic ion may be independently gauged from its magnetic susceptibility as there will be a considerable variation in the susceptibility value in case of a change of valence. Chromium, which is a transitional element, has 3 unpaired electrons in chromic compounds (the corresponding Bohr magneton value is 3.7) and 4 unpaired electrons in case of chromous compounds. Provided ionic bonding is retained in the formation of its compounds, the Cr^{+2} will exhibit its full Bohr magneton value of 4.9.

In the present work, the measurements were done in solution. As the magnetic pull was found to be too feeble to be measured accurately by Guoy's method with an ordinary analytical balance, Dutta's[8] method using a torsion balance was adopted for the purpose. The reaction mixture was prepared by adding aqueous acidified chromate to a carbazide solution (in 1:1 ethylene glycol-*iso*-propyl alcohol mixture) in the proportion of 2:3 (that of the maximum composition in Job's method), wherein as a first approximation it could be assumed that the conversion of the chromate to the coloured Cr^{+2} compound was complete.

DISCUSSION

The molar susceptibility value of 4.6 Bohr magnetons of the compound calculated from the observed data on the assumption of 1:1 chromous-carbazone ratio, confirms the presence of Cr^{+2} ion in the complex. The binding between the Cr^{+2} ion and the organic addenda may, then, be considered to be primarily ionic. It may be pointed out in this connection that in most of the chromous complexes[9], excepting the very characteristic chromocyanide, the ionic bonding has been found to be retained. Thus, magnetic measurements also corroborate the formation of an inner complex salt of bivalent chromium. From such a conclusion, it must be considered that, to preserve the electroneutrality of the compound, both the H atoms in the carbazone molecule are active in salt formation. But ordinarily carbazone has only one active H (keto form)[10] and this anomaly can only be explained if the carbazone molecule is supposed to be reactive in its enolic form, in which case two H atoms are available. The formation of the coloured compound may then be represented as follows,



enol form complex.

where Cr^{+2} ion forms a part of the 5 membered ring structure and it may be considered to be the reason of the unusual stability of this compound in comparison with other chromous compounds.

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SUMMARY

Job's method was employed for ascertaining the detailed mechanism of the chromate-carbazide reaction. Three different systems (1) chromate-carbazide,

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(2) chromate-carbazone and (3) chromous-carbazone, leading to the formation of the same coloured complex were investigated. From studies in equimolecular solutions, the maximum composition values for these reactions were found to be 2:3, 1:3 and 1:1, respectively. Proceeding from the assumption that the reaction (3) is a case of simple displacement, the stoichiometry of all the three systems has been formulated. The role of chromate in the chromate-carbazide reaction, has been found to be primarily that of an oxidising agent followed by complex formation. The tentative formulation for the three systems is given below.

$$(1)\quad 2Cr^{+6}+3\ \text{carbazide} \rightleftharpoons 2\begin{bmatrix}Cr^{+2}\ \text{carbazone}^{-2}\\ \text{complex}\end{bmatrix} + \text{carbadiazone} + 4\ H^{+}$$

$$(2)\quad Cr^{+6} + 3\ \text{carbazone} \rightleftharpoons \begin{bmatrix}Cr^{+2}\ \text{carbazone}^{-2}\\ \text{complex}\end{bmatrix} + 2\ \text{carbadiazone} + 2\ H^{+}$$

$$(3)\quad Cr^{+2} + \text{carbazone} \rightleftharpoons \begin{bmatrix}Cr^{+2}\ \text{carbazone}^{-2}\\ \text{complex}\end{bmatrix} + 2\ H^{+}$$

The proposed mechanism seems to explain the relevant facts observed in the course of investigation of the three systems, particularly the rapid discharge of the colour produced when excess of chromium was added and the greater sensitivity of carbazide as compared to carbazone were accounted for.

The determination of K values from studies in non-equimolecular solutions of the three reactions also corroborates the aforesaid mechanism. The apparent dissociation constant of the Cr^{+2}-carbazone complex was found to be $2.7 \cdot 10^{-6}$ and the equilibrium constants of (1) and (2) were calculated as $5.7 \cdot 10^{-12}$ and $2.3 \cdot 10^{-7}$, respectively. The existence of bivalent Cr^{+2} ion in the complex molecule has also been independently confirmed from magnetochemical measurements. The molar susceptibility value of 4.6 Bohr magnetons calculated on the basis of 1:1 chromous-carbazone ratio, indicates ionic bonding in the complex.

RÉSUMÉ

La méthode de Job a été utilisée pour étudier en détail le mécanisme de la réaction chromate-carbazide. Les trois systèmes: (1) chromate-carbazide, (2) chromate-carbazone et (3) chrome (II)-carbazone, conduisant à la formation du même complexe coloré, ont été examinés. En solutions équimoléculaires, les valeurs de composition maximum pour ces réactions seraient 2:3, 1:3 et 1:1 respectivement. Supposant que la réaction (3) consiste en un simple déplacement, la stoechiométrie des 3 systémes a été formulée. Le rôle du chromate dans la réaction chromate-carbazide semble être en premier lieu celui d'un agent oxydant, formant ensuite un complexe. Les équations suivantes sont proposées pour les 3 systèmes:

$$(1)\quad 2\ Cr^{+6} + 3\ \text{carbazide} \rightleftharpoons 2\ [Cr^{+2}\ \text{carbazone}^{-2}] + \text{carbadiazone} + 4\ H^{+}$$

$$(2)\quad Cr^{+6} + 3\ \text{carbazone} \rightleftharpoons [Cr^{+2}\ \text{carbazone}^{-2}] + 2\ \text{carbadiazone} + 2\ H^{+}$$

$$(3)\quad Cr^{+2} + \text{carbazone} \rightleftharpoons [Cr^{+2}\ \text{carbazone}^{-2}] + 2\ H^{+}$$

Le mécanisme proposé semble expliquer les phénomènes observés au cours de l'étude des 3 systèmes, en particulier la disparition de la coloration produite lorsqu'on est en présence d'un excès de chrome et la plus grande sensibilité de la carbazide comparée à la carbazone. La détermination des valeurs de K en solutions équimoléculaires de ces 3 réactions confirme le mécanisme adopté. La constante de dissociation apparente du complexe Cr^{+2}-carbazone est égale à $2.7 \cdot 10^{-6}$ et les constantes d'équilibre de (1) et (2) à $5.7 \cdot 10^{-12}$ et $2.3 \cdot 10^{-7}$ respectivement. L'existence de l'ion Cr^{+2} dans la molécule complexe a été prouvée indépendamment, par les mesures magnétochimiques. La valeur de la susceptibilité moléculaire de 4.6 Bohr magnétons, calculée en se basant sur le rapport chrome(II)-carbazone 1:1, indique une liaison ionique dans le complexe.

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ZUSAMMENFASSUNG

Die Methode von JOB wurde zur Ermittlung des eingehenden Mechanismus der Chromat-Carbazid-Reaktion verwendet. Drei verschiedene zur Bildung desselben gefärbten Komplexes führende Systeme, (1) Chromat-Carbazid, (2) Chromat-Carbazon und (3) Chrom-II-Carbazon wurden untersucht. Bei Studien in äquimolekularen Lösungen wurden die Werte für die maximale Zusammensetzung dieser Reaktionen zu 2:3, 1:3 bzw. 1:1 gefunden. Ausgehend von der Annahme, dass die Reaktion (3) eine einfache Verdrängung darstellt, wurden die drei Systeme stöchiometrisch formuliert. Wie gefunden wurde spielt Chromat bei der Chromat-Carbazid-Reaktion hauptsächlich die Rolle eines Oxydationsmittels; darauf erfolgt Komplexbildung. Die versuchsweise Formulierung der drei Systeme wird unten gegeben.

$$(1)\quad 2\ Cr^{+6} + 3\ \text{Carbazid} \rightleftharpoons 2[Cr^{+2}\ \text{Carbazon}^{-2}\ \text{Komplex}] + \text{Carbadiazon} + 4H^{+}$$

$$(2)\quad Cr^{+6} + 3\ \text{Carbazon} \rightleftharpoons [Cr^{+2}\ \text{Carbazon}^{-2}\ \text{Komplex}] + 2\ \text{Carbadiazon} + 2H^{+}$$

$$(3)\quad Cr^{+2} + \text{Carbazon} \rightleftharpoons [Cr^{+2}\ \text{Carbazon}^{-2}\ \text{Komplex}] + 2H^{+}$$

Der vorgeschlagene Mechanismus scheint die im Laufe der Untersuchung der drei Systeme beobachteten Tatsachen zu erklären; besonders die rasche Entfärbung der durch einen Zusatz überschüssigen Chroms erzeugten Farbe und die verglichen mit dem Carbazone grössere Empfindlichkeit des Carbazids liess sich so erklären.

Die Bestimmung der *K*-Werte aus Untersuchungen der drei Reaktionen in nichtäquimolekularen Lösungen bestätigt ebenfalls diesen obenerwähnten Mechanismus. Die scheinbare Dissoziationskonstante des Cr^{+2}-Carbazon-Komplexes wurde zu $2.7 \cdot 10^{-6}$ gefunden und die Gleichgewichtskonstanten von (1) und (2) wurden zu $5.7 \cdot 10^{-12}$ bzw. $2.3 \cdot 10^{-7}$ berechnet. Das Vorkommen von zweiwertigen Cr^{+2} im Komplexmolekül wurde unabhängig davon durch magneto-chemische Messungen bestätigt. Der auf Grund des Verhältnisses von 1:1 des Cr-II-Carbazons berechnete Wert der molaren Susceptibilität für 4.6 Bohr'sche Magnetonen zeigt eine Ionenbindung im Komplex an.

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ANALYTISCHE AUSWERTUNG VON AUSTAUSCHREAKTIONEN ZWISCHEN LÖSLICHEN UND WENIG LÖSLICHEN ELEKTROLYTEN

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EINLEITUNG

Sowohl qualitative als auch quantitative analytische Methoden, die Reaktionen folgender Art

$$\begin{array}{cccc} \mathrm{e}\ A_mB_n & +\ \mathrm{f}\ C_oD_p & \rightleftharpoons \mathrm{g}\ A_qD_r & +\ \mathrm{h}\ C_sB_t \\ \text{fest} & \text{gelöst} & \text{fest} & \text{gelöst} \end{array}$$

zur Grundlage haben, sind sehr zahlreich. Die Tabelle I, die keine Vollständigkeit anstrebt, enthält eine Übersicht der Arbeit, die auf diesem Gebiete schon geleistet wurde. Die Wiederholung eines Teiles des darüber veröffentlichten Materials hat mich überzeugt, dass ein theoretisches und praktisches Studium der obigen Reaktionen wünschenswert wäre, das bezüglich der Spezifität der Reaktionen analytischen Methoden dieser Art grössere Sicherheit geben würde. Ausserdem scheint es möglich eine grosse Zahl von Reaktionen vorauszusagen, die in der chemischen Literatur noch nicht behandelt wurden.

THEORETISCHER TEIL

In der Suspension eines in Wasser schwer löslichen Elektrolyten besteht ein Gleichgewicht zwischen dem festen und dem gelösten Anteil, welch letzterer praktisch stets als völlig ionisiert betrachtet werden kann:

$$\begin{array}{ccc} A_mB_n & \rightleftharpoons A_mB_n & \rightarrow mA^* + nB^* \\ \text{fest} & \text{gelöst} & \end{array}$$

In dieser und in den folgenden Gleichungen bezeichnen die Sternchen Ionen, ohne Rücksicht auf Vorzeichen und Ladungszahl.

Die Konzentration der Ionen in der Lösung folgt ungefähr der Gleichung

$$[A^*]^m . [B^*]^n = L_1 \tag{a}$$

TABELLE I

LITERATURÜBERSICHT DER REAKTIONEN ZWISCHEN LÖSLICHEN UND WENIG LÖSLICHEN ELEKTROLYTEN

	Reaktion	Anwendung	Liter.
1.	$AgJO_3 + Cl^- \rightleftharpoons AgCl + JO_3^-$	Bestimmung von Cl^-	32
2.	$AgCl + KCNS \rightleftharpoons AgCNS + KCl$	Interferenz im Volhard-Verf.	38
3.	$4AgCl + K_4[Fe(CN)_6] \rightleftharpoons Ag_4[Fe(CN)_6] + 4KCl$	Nachweis von AgCl und Cl^-	7,34
4.	$Ag_4[Fe(CN)_6] + 4X^- \rightleftharpoons 4AgX + [Fe(CN)_6]^{-4}$	Nachw. v. Cl^-, Br^-, J^-, CN^-, CNS^-, $[Fe(CN)_6]^{-3}$	9,20
5.	$Ag_3[Fe(CN)_6] + 3CNS^- \rightleftharpoons 3AgCNS + [Fe(CN)_6]^{-3}$		20
6.	$Ag_2CrO_4 + 2X^- \rightleftharpoons 2AgX + CrO_4^{-2}$	Nachw. v. Cl^-, Br^-, J^-, CNS^-	10,32
7.	$Ag_2C_2O_4 + 2Cl^- \rightleftharpoons 2AgCl + C_2O_4^{-2}$	Bestimmung von Cl^-	32
8.	$Ag_2CO_3 + 2X^- \rightleftharpoons 2AgX + CO_3^{-2}$	Nachweis von Halogenen	4
9.	$Ag_3PO_4 + 3NaCl \rightleftharpoons 3AgCl + Na_3PO_4$	Bestimmung von PO_4^{-3}	29
10.	$BaCO_3 + Na_2SO_4 \rightleftharpoons BaSO_4 + Na_2CO_3$	Nachweis von SO_4^{-2}	3,2
11.	$BaCO_3 + K_2CrO_4 \rightleftharpoons BaCrO_4 + K_2CO_3$		30
12.	$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4$	Aufschliessung von Barit	1
13.	$BaSO_4 + CrO_4^{-2} \rightleftharpoons BaCrO_4 + SO_4^{-2}$	Oberflächenbestimmung von $BaSO_4$	23,30
14.	$BaC_2O_4 + Na_2SO_4 \rightleftharpoons BaSO_4 + Na_2C_2O_4$	Bestimmung von SO_4^{-2}	28
15.	$Ba(JO_3)_2 + Na_2SO_4 \rightleftharpoons BaSO_4 + 2NaJO_3$	Bestimmung von SO_4^{-2}	35
16.	$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$	Unterscheidung zwischen Gypsit und Anhydrit	11
17.	$CaSO_4 + Pb^{+2} \rightleftharpoons PbSO_4 + Ca^{+2}$	Nachweis von $CaSO_4$	8
18.	$CaF_2 + Na_2C_2O_4 \rightleftharpoons CaC_2O_4 + 2NaF$	Interferenz in einer Titrimetrischen Methode für F^-	31
19.	$H_4MoO_3.Fe(CN)_6 + 2Zn^{+2} \rightleftharpoons Zn_2[Fe(CN)_6] + MoO_3 + 4H^+$	Nachweis von Zn in Mineralen	12
20.	$MeO + 2NaHCO_3 \rightleftharpoons MeCO_3 + Na_2CO_3 + H_2O$	Nachweis von Oxyden	33
21.	$PbS + 2AgNO_3 \rightleftharpoons Ag_2S + Pb(NO_3)_2$	Nachweis von schwerlöslichen Sulfiden	26

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wobei L_1 das Löslichkeitsprodukt der Substanz A_mB_n ist. Da

$$n[A^*] = m[B^*] \tag{b}$$

ist, so kann man auch schreiben

$$\left(\frac{n}{m}\right)^n [A^*]^{m+n} = L_1 \tag{c}$$

Fügt man zu der Suspension von A_mB_n einen löslichen Elektrolyten C_oD_p hinzu, der eine wenig lösliche Verbindung A_qD_r zu bilden vermag, so stellt sich ein Gleichgewicht folgenden Typs ein:

$$\underset{\text{fest}}{eA_mB_n} + \underset{\text{gelöst}}{f\,C_oD_p} \rightleftarrows \underset{\text{fest}}{g\,A_qD_r} + \underset{\text{gelöst}}{h\,C_sB_t}$$

sofern die Konzentration der Ionen D* hoch genug ist, um der Beziehung

$$[D^*]^r = \frac{L_2}{[A^*]^q} \tag{d}$$

zu genügen. L_2 ist das Löslichkeitsprodukt von A_qD_r.

Da die Konzentration der Ionen A* in der Gleichung (d) durch die Beziehung (c) bestimmt wird, ergibt sich

$$[D^*] = \left(\frac{n}{m}\right)^{\frac{nq}{(m+n)r}} \frac{L_2^{\frac{1}{r}}}{L_1^{\frac{q}{(m+n)r}}} \tag{e}$$

Diese Gleichung zeigt, dass die Reaktion eintritt, gleichgültig, ob das Löslichkeitsprodukt (oder die Löslichkeit) der schwer löslichen Substanz A_mB_n grösser oder kleiner als das des durch die Reaktion gebildeten Stoffes ist. Die Reaktion ist nur dann unmöglich, wenn die Löslichkeit des Elektrolyten C_oD_p es nicht gestattet, die Konzentration des Ions D*, die von der Gleichung (e) verlangt wird, zu erreichen.

Wenn man die Möglichkeit einer Reaktion des beschriebenen Typs durch die Errechnung des Wertes von [D*] nach Gleichung (e) bestimmt, darf man nicht vergessen, dass das Resultat nur annähernd der Wahrheit entspricht, wenn man Löslichkeitsprodukte einsetzt, die in reinem Wasser bestimmt wurden. Da im vorliegenden Falle immer zumindest zwei Elektrolyten in der Lösung vorhanden sind, müsste man Aktivitäten statt der Konzentrationen benützen, um die Anziehung zwischen den Ionen zu berücksichtigen. Der Unterschied zwischen der theoretischen Mindestmenge des Ions D*, die für die Reaktion nötig ist, und der Menge, die man zusetzen muss, um ihre Beobachtung zu ermöglichen, ist aber meist so gross, dass der Fehler, der durch Benützung von Konzentrationen an

Stelle von Aktivitäten verursacht wird, vernachlässigt werden kann. Deshalb genügt die Kenntniss der Grössenordnung des Wertes von [D*].

Andere Effekte, die die Löslichkeit von festen Elektrolyten beeinflussen können, sind das pH des Milieus, die Bildung von Komplexen und die Grösse der Teilchen[13].

EXPERIMENTELLER TEIL

1. Die Reaktionen von FEIGL UND SEBOTH (Tabelle I, 8 und 10) identifizieren die betreffenden Ionen durch die Reaktion der Karbonate auf Phenolphtalein. Ihre Verallgemeinerung, durch die Benützung verschiedener wenig löslicher Karbonate, wurde nun unternommen. In Tabelle II werden die Erfassungsgrenzen, die durch das unten angegebene Verfahren bestimmt wurden, mit den Werten verglichen, die mit Hilfe der obigen theoretischen Gleichung berechnet wurden.

Reagenzien

$CaCO_3$, $BaCO_3$, $PbCO_3$, Ag_2CO_3, analysenrein, durch Fällung hergestellt. 1%-ige Phenolphtaleinlösung in 50 %-igem Alkohol.

Verfahren

Man bringt auf eine Tüpfelplatte etwas von dem wenig löslichen Karbonat, einen Mikrotropfen der Phenolphtaleinlösung und einen Tropfen der Probelösung (die vorher zum Phenolphtalein-Endpunkt neutralisiert worden war). Das Auftreten einer roten Färbung ist als positive Reaktion zu betrachten.

Der Vergleich mit einer Blindprobe, der immer ratsam ist, muss besonders bei Anwendung von leicht hydrolysierbaren[18] Karbonaten durchgeführt werden, die eine schwache Rotfärbung zeigen.

Anwendungen

Durch obiges Verfahren lassen sich folgende Anionen bis zu den nachstehenden Erfassungsgrenzen und Grenzverdünnungen nachweisen:

$CaCO_3$	Oxalat	2.5 γ	1 : 20,000
	Fluorid	5 γ	1 : 10,000
$BaCO_3$	Sulfat	2 γ	1 : 25,000
	Chromat	3 γ	1 : 16,000
$PbCO_3$	Chromat	5 γ	1 : 10,000
	Phosphat	10 γ	1 : 5,000
Ag_2CO_3	Chlorid	1 γ	1 : 50,000
	Bromid	1 γ	1 : 50,000
	Jodid	1 γ	1 : 50,000
	Phosphat	8 γ	1 : 6,250

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TABELLE II

ERFASSUNGSGRENZEN VERSCHIEDENER IONEN DURCH IHRE REAKTION MIT EINEM WENIGLÖSLICHEN KARBONAT UND PHENOLPHTALEIN

A_mB_n	L_1	D^-	L_2	Minimalkonzentration von D^-		
				theoretisch		experimentell
				Mol/l	γ/0.05 ml	γ/0.05 ml
$CaCO_3$	$0.9\cdot10^{-8}$	F^-	$3.9\cdot10^{-11}$	$6.5\cdot10^{-4}$	0.6	5
		J^-				11500 negativ
		JO_3^-	$6.4\cdot10^{-7}$	$8.2\cdot10^{-2}$	720	1000
		BrO_3^-				1500
		SO_4^{-2}	$6.1\cdot10^{-5}$	$6.4\cdot10^{-1}$	3100	50
		CrO_4^{-2}	$2.3\cdot10^{-2}$	$2.4\cdot10^{2}$	$1.4\cdot10^{6}$	negativ
		$C_2O_4^{-2}$	$2.6\cdot10^{-9}$	$2.7\cdot10^{-5}$	0.1	2.5
		PO_4^{-3}				300 negativ
$BaCO_3$	$0.8\cdot10^{-8}$	F^-	$1.7\cdot10^{-6}$	$1.4\cdot10^{-1}$	131	25
		J^-				11500 negativ
		JO_3^-	$6.5\cdot10^{-10}$	$2.7\cdot10^{-3}$	23.5	90
		BrO_3^-	$3.2\cdot10^{-5}$	0.6	3800	300
		SO_4^{-2}	$1.0\cdot10^{-10}$	$1.1\cdot10^{-6}$	0.005	2
		CrO_4^{-2}	$2.4\cdot10^{-10}$	$2.7\cdot10^{-6}$	0.015	3
		$C_2O_4^{-2}$	$2.0\cdot10^{-7}$	$2.2\cdot10^{-3}$	9.8	25
		PO_4^{-3}				35
$PbCO_3$	$3.3\cdot10^{-14}$	F^-	$3.7\cdot10^{-8}$	0.45	428	200 negativ
		Cl^-	$1.0\cdot10^{-4}$	23.4	41500	8000 negativ
		Br^-	$6.3\cdot10^{-6}$	5.8	23500	8000 negativ
		J^-	$1.4\cdot10^{-8}$	0.3	1750	7650
		JO_3^-	$2.6\cdot10^{-13}$	$1.2\cdot10^{-3}$	10.5	4080
		BrO_3^-	$1.0\cdot10^{-4}$	23.5	150000	3830 negativ
		SO_4^{-2}	$1.1\cdot10^{-8}$	$5.8\cdot10^{-2}$	280	negativ
		CrO_4^{-2}	$1.8\cdot10^{-14}$	$1.0\cdot10^{-7}$	$5.8\cdot10^{-4}$	5
		$C_2O_4^{-2}$	$2.7\cdot10^{-11}$	$1.5\cdot10^{-4}$	0.66	200
		PO_4^{-3}	$1.5\cdot10^{-32}$	$1.6\cdot10^{-6}$	$7.6\cdot10^{-4}$	10
Ag_2CO_3	$8.2\cdot10^{-12}$	F^-				200 negativ
		Cl^-	$1.7\cdot10^{-10}$	$6.7\cdot10^{-7}$	0.001	1
		Br^-	$3.3\cdot10^{-13}$	$1.3\cdot10^{-9}$	$5.2\cdot10^{-6}$	1
		J^-	$1.5\cdot10^{-16}$	$5.9\cdot10^{-13}$	$3.7\cdot10^{-9}$	1
		JO_3^-	$2.2\cdot10^{-8}$	$8.6\cdot10^{-5}$	0.757	30
		BrO_3^-	$5.8\cdot10^{-5}$	$2.3\cdot10^{-1}$	1460	2500
		SO_4^{-2}	$1.2\cdot10^{-5}$	$1.8\cdot10^{2}$	890000	negativ
		CrO_4^{-2}	$1.1\cdot10^{-12}$	$1.7\cdot10^{-5}$	0.098	20
		$C_2O_4^{-2}$	$1.3\cdot10^{-11}$	$2.0\cdot10^{-4}$	0.886	50
		PO_4^{-3}	$1.8\cdot10^{-18}$	$1.1\cdot10^{-7}$	$5.2\cdot10^{-4}$	8

Die Löslichkeitsprodukte dieser und der folgenden Tabellen stammen hauptsächlich aus LANGE[27].

Ausserdem geben mit Silberkarbonat noch folgende Anionen eine empfindliche Reaktion: Arseniat, Cyanid, Ferro- und Ferricyanid, Rhodanid.

Die Reaktion ist also ziemlich selektiv und erlaubt den Nachweis von einem oder mehr Anionen einer kleinen Gruppe. Die für die Erfassungsgrenzen bestimmten Werte hängen etwas von der Menge und der Beschaffenheit des wenig löslichen Karbonats und von der Reaktionsdauer ab und sind deshalb nicht leicht zu reproduzieren.

Interferenzen

Obige Reaktionen sind aber nur dann genügend selektiv, wenn die gesamte Anionenkonzentration der Lösung 20γ /0.05 ml nicht übersteigt. Von dieser Konzentration an reagieren viele Anionen mit den wenig löslichen Karbonaten (Tabelle II).

Die Probelösung darf auch an selbst völlig indifferenten Elektrolyten nicht zu reich sein. Grosse Ionenkonzentrationen setzen die an sich schon kleine Löslichkeit der Karbonate herab und verhindern die Reaktion. So gibt zum Beispiel eine $0.05N$-e Sulfatlösung, bei Zusatz des gleichen Volumens Wasser eine sehr starke Rotfärbung mit Bariumkarbonat. Dieselbe Sulfatlösung gibt aber nach Zusatz des gleichen Volumens einer 25 %-igen Natriumchloridlösung eine völlig negative Reaktion. Wenn man diese Lösung mit Wasser verdünnt (2 : 5), erscheint die Rotfärbung in gleicher Intensität in beiden Fällen. Einen identischen Effekt kann man mit den Systemen $CaCO_3$-Oxalat-Chlorid und $CaCO_3$-Oxalat-Tartrat beobachten.

2. Die in vorliegender Mitteilung behandelten Austauschreaktionen ermöglichen mittels Musterung der Löslichkeitsprodukte und der Ausführung einer einfachen Rechnung das Entwerfen von spezifischen oder selektiven Identitätsprüfungen.

So, zum Beispiel, zeigt die Tabelle III, dass die Reaktion

$$AgCNS + D^- \rightleftarrows AgD + CNS^-$$

sehr empfindlich für Jodid und Bromid, aber weniger empfindlich für Chlorid ist. Sie könnte also zur Unterscheidung dieser Anionen dienen. Um die Interferenz anderer Ionen zu vermeiden, muss man in saurem Milieu arbeiten.

TABELLE III

ERFASSUNGSGRENZEN VERSCHIEDENER IONEN DURCH IHRE REAKTION MIT SILBERRHODANID UND FERRISALZ

A_mB_n	L_1	D^-	L_2	Minimalkonzentration von D^-		
				theoretisch		experimentell
				Mol/l	γ/0.05 ml	γ/0.05 ml
AgCNS	$1.0 \cdot 10^{-12}$	J^-	$1.5 \cdot 10^{-16}$	$1.5 \cdot 10^{-10}$	$0.9 \cdot 10^{-6}$	0.3
		Br^-	$3.3 \cdot 10^{-13}$	$3.3 \cdot 10^{-7}$	$1.1 \cdot 10^{-3}$	0.3
		Cl^-	$1.7 \cdot 10^{-10}$	$1.7 \cdot 10^{-4}$	0.3	15
		CN^-				60
		JO_3^-	$2.2 \cdot 10^{-8}$	$2.2 \cdot 10^{-2}$	$1.9 \cdot 10^{2}$	1750 negativ

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Reagenzien

Silberrhodanid. Dieses Reagens kann man herstellen, indem man zu einer ungefähr 0.1*N*-en Silbernitratlösung, die einige Tropfen einer mit Schwefelsäure angesäuerten Eisen-III-sulfatlösung enthält, solange eine ungefähr 0.1*N*-e Ammoniumrhodanidlösung hinzufügt, bis eine schwache Rotfärbung auftritt. Der Niederschlag wird durch Abschleudern separiert, muss nicht getrocknet werden und ist im Dunkeln aufzubewahren. Schwefelsaure Ferrisulfatlösung.

Verfahren

Man bringt auf eine Tüpfelplatte etwas Silberrhodanid, einen Tropfen der Probelösung und einen Tropfen der sauren Eisensulfatlösung. Das Auftreten der roten Eisenrhodanidfärbung weist auf eine positive Reaktion hin.

Anwendungen

Durch obiges Verfahren lassen sich folgende Anionen bis zu den nachstehenden Erfassungsgrenzen und Grenzverdünnungen nachweisen:

Bromid	0.2 γ	1 : 250,000
Jodid	0.2 γ	1 : 250,000

Interferenzen

Chlorid beginnt eine Rotfärbung zu geben, wenn seine Konzentration in der Probelösung 15 γ/0.05 ml überschreitet.

Im Beisein von bedeutenden Mengen von Phosphaten, Arseniaten, Oxalaten, Tartaraten und anderen organischen Hydroxylverbindungen, Fluoriden, Mercurisalzen und vielen anderen Substanzen die Komplexbildner für Ferriionen sind, könnten diese letztgenannten zur Prüfung auf freies Rhodanidion nicht verwendet werden[5]. Da aber in der Probelösung keine bedeutenden Mengen von selbst indifferenten Elektrolyten vorhanden sein dürfen (siehe oben) und da die Ferrikonzentration hoch ist oder beliebig gesteigert werden kann, hindert keine dieser Substanzen ernstlich die beschriebene Identitätsprüfung.

In Gegenwart von Nitritionen kann eine Rotfärbung, durch Bildung von Nitrosilrhodanid, selbst ohne Ferrisalz, auftreten[5]. Ionen die gefärbte Ferri-Verbindungen geben, erschweren oder verhindern die Beobachtung des Versuches. In solchen Fällen muss man eine andere Probe auf Rhodanid wählen.

3. Die unter Nummer 2 beschriebene Reaktion kann als Grundlage einer spezifischen Identitätsprüfung für Bromidionen dienen. Erinnern wir uns, dass, wenn die beschriebenen Bedingungen erfüllt sind, Silberrhodanid nur in Silberbromid und Jodid verwandelt werden kann. Da das Silberbromid lichtempfindlicher ist als das Silberjodid oder Rhodanid, ist es möglich, die erstgenannten Ionen durch das Dunkelwerden der Mischung nachzuweisen.

Zum Erfolge dieser Probe trägt der Umstand bei, dass das freie Rhodanidion (durch die Reaktion gebildet) die Photo-Zersetzung des Silberbromids so beschleunigt und verstärkt, dass diese schon bei diffusem Lichte leicht beobachtet werden kann. Es handelt sich wahrscheinlich um einen katalytischen Vorgang. 0.1 γ Rhodanid in 0.05 ml üben noch einen sichtbaren Einfluss auf Silberbromid aus.

Reagenz

Silberrhodanid. Dieses Reagens kann man herstellen, indem man zu einer ungefähr 0.1N-en Silbernitratlösung langsam etwas mehr als das gleiche Volumen einer Ammoniumrhodanidlösung derselben Normalität hinzufügt. Der Niederschlag wird durch Abschleudern gewonnen, dreimal mit Wasser gewaschen, muss nicht getrocknet werden und ist im Dunkeln aufzubewahren.

Verfahren

Man bringt auf eine Tüpfelplatte etwas Silberrhodanid und einen Tropfen der Probelösung. Man erlaubt dieser Mischung eine Reaktionszeit von rund einer Minute im Dunkeln und exponiert dann in diffusem Licht. Ein rascheres und intensiveres Dunkelwerden als im Leerversuch weist auf eine positive Reaktion hin.

Anwendungen

Durch obiges Verfahren lässt sich das Bromidion bis zu der nachstehenden Erfassungsgrenze und Grenzverdünnung nachweisen:

Bromid	5 γ	1 : 10,000

Interferenzen

Chlorid beeinflusst die Probe auf Bromid, wenn seine Konzentration in der zu untersuchenden Lösung 150 γ/0.05 ml überschreitet. Selbst 750 γ Chlorid in 0.05 ml geben jedoch nur eine Reaktion, deren Intensität mit der von 5 γ Bromid gegebenen verglichen werden kann. Dieser Umstand ermöglicht es mit einiger Praxis die Identifizierung von Bromidionen in Gegenwart beträchtlicher Mengen Chlorid durchzuführen.

Im Beisein von Jodid ist die Empfindlichkeit der Reaktion kleiner, da die intensive Gelbfärbung des Silberjodids die Beobachtung des Vorganges erschwert.

4. Ein weiterer Vorteil, den Austauschreaktionen zwischen löslichen und wenig löslichen Elektrolyten aufweisen, ist die Möglichkeit, Ionen, für die es nur komplizierte oder zweifelhafte qualitative (oder quantitative) Bestimmungsreaktionen gibt, in andere umzuwandeln, deren Nachweis einfacher oder sicherer ist. Manchmal kann eine solche Umwandlung auch vom Standpunkt der Sensibilität der Reaktion interessant sein. So zum Beispiel zeigte FEIGL[6], dass die Empfindlichkeit der Reaktion für Jodid

$$J^- + X^+ \rightarrow J^\circ$$

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durch seine Oxydation in Jodat sechsfach gesteigert werden kann, denn ein Mol Jodid gibt ein Mol Jodat, und dieses setzt sechs Jodatome frei, im Sinne der Reaktionsgleichung:

$$JO_3^- + 5\ J^- + 6\ H^+ \rightarrow 3\ J_2 + 3\ H_2O$$

Die Umwandlung von Jodid in Jodat könnte auch durch die Austauschreaktion

$$AgJO_3 + J^- \rightleftarrows AgJ + JO_3^-,$$

die praktisch quantitativ ist[32], erzielt werden.

Um die beschriebenen Vorteile zu erläutern wurde Jodation ausgesucht, dessen Nachweis sehr einfach ist. Als Quelle dieses kann man Bleijodat (in neutralem Milieu) und Silberjodat (in saurem Milieu, um die Interferenz verschiedener Ionen, die in neutraler Lösung schwer lösliche Silbersalze geben, zu vermeiden) benützen. Die Tabelle IV zeigt die Löslichkeitsverhältnisse, die in diesen Serien von wenig löslichen Elektrolyten vorherrschen. Die Löslichkeitsprodukte, die für die Silbersalze angegeben sind, beziehen sich auf reines Wasser als Lösungsmittel. Da wir aber in saurem Milieu arbeiten, sind diese Werte teilweise recht weit von der Wahrheit entfernt, und werden hier nur zu Vergleichszwecken angegeben.

TABELLE IV

ERFASSUNGSGRENZEN VERSCHIEDENER IONEN DURCH IHRE REAKTION MIT WENIGLÖSLICHEN JODATEN, KJ UND SÄURE

A_mB_n	L_1	D^-	L_2	Minimalkonzentration von D^-		
				theoretisch		experimentell
				Mol/l	γ/0.05 ml	γ/0.05 ml
$Pb(JO_3)_2$	$2.6 \cdot 10^{-13}$	PO_4^{-3}	$1.5 \cdot 10^{-32}$	$4.8 \cdot 10^{-10}$	$2.3 \cdot 10^{-6}$	1
		$C_2O_4^{-2}$	$2.7 \cdot 10^{-11}$	$6.8 \cdot 10^{-7}$	$3.0 \cdot 10^{-3}$	1
		SO_4^{-2}	$1.1 \cdot 10^{-8}$	$2.6 \cdot 10^{-4}$	1.3	40
$AgJO_3$	$2.2 \cdot 10^{-8}$	Cl^-	$1.7 \cdot 10^{-10}$	$1.1 \cdot 10^{-6}$	$2.0 \cdot 10^{-3}$	0.5
		Br^-	$3.3 \cdot 10^{-13}$	$2.2 \cdot 10^{-9}$	$8.9 \cdot 10^{-6}$	0.5
		J^-	$1.5 \cdot 10^{-16}$	$1.0 \cdot 10^{-12}$	$6.4 \cdot 10^{-9}$	0.3
		$C_2O_4^{-2}$				200 negativ
		PO_4^{-3}				300 negativ

Reagenzien

$Pb(JO_3)_2$, $AgJO_3$, analysenrein
50 %-ige Kaliumjodidlösung
3*N*-e Schwefelsäure

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Verfahren

Man bringt auf eine Tüpfelplatte etwas von dem wenigløslichen Jodat und einen Tropfen der Probelösung (neutral im Falle des Bleijodats und mit Schwefelsäure leicht angesäuert im Falle des Silberjodats). Nach guter Vermischung lässt man die Flüssigkeit in einem Filtrierpapier durch Kapillarität hochsteigen. Auf die feuchte Stelle des Papiers gibt man nun einen Tropfen der Kaliumjodidlösung einen Tropfen der verdünnten Schwefelsäure. Die braune Jodfarbe oder eine stärkere Blaufärbung als in der Blindprobe weist auf eine positive Reaktion hin.

Anwendungen

Durch obiges Verfahren lassen sich folgende Anionen bis zu den nachstehenden Erfassungsgrenzen und Grenzverdünnungen nachweisen:

$Pb(JO_3)_2$	Phosphat	1 γ	1 : 50,000
	Oxalat	1 γ	1 : 50,000
$AgJO_3$	Chlorid	0.5 γ	1 : 100,000
	Bromid	0.5 γ	1 : 100,000
	Jodid	0.3 γ	1 : 165,000

DISKUSSION

1. Das Ergebniss des im theoretischen Teile ausgeführten Gedankenganges steht im Gegensatz zu jenen Texten (vgl. beispielsweise neben vielen anderen[17]), die angeben, dass eine wenig lösliche Substanz C nur dann durch die Reaktion eines löslichen Elektrolyts A mit einem wenig löslichen Elektrolyten B gebildet werden kann, wenn das Löslichkeitsprodukt (oder die Löslichkeit) von C kleiner ist als das von B. Serien von Ionen, die der löslichen Substanz angehören, werden als nicht reaktiv bezeichnet, oft, weil die Autoren scheinbar nicht mit genug konzentrierten Lösungen gearbeitet haben.

So, zum Beispiel, wurde im praktischen Teile dieser Arbeit die FEIGL UND SEBOTH'sche Reaktion (Tabelle I, 10), die als spezifisch für Sulfat angeführt wird (nur Silicofluorid soll interferieren), näher untersucht. Es wurde festgestellt, dass ausserdem noch Chromat, Jodat, Oxalat, Phosphat, Bromat, Fluorid und höchstwahrscheinlich noch andere Ionen, die nicht geprüft wurden, im Stande sind Karbonation aus Bariumkarbonat zu befreien. Unter den aufgezählten Ionen haben nur Bariumchromat und Jodat kleinere Löslichkeitsprodukte als Bariumkarbonat.

Die Erfassungsgrenzen, in diesem und in analogen Fällen, sind aber meist zu hoch, um die Bestimmung der Ionen, die schwererlösliche Niederschläge geben, ernsthaft zu stören (Tabellen II, III und IV).

2. Die Werte der Tabellen II, III und IV zeigen, in den meisten Fällen, gute Übereinstimmung zwischen der berechneten und der experimentellen Mindest-

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konzentration des Ions des leicht löslichen Elektrolyten, die nötig ist, um die Reaktion zu beginnen. Dass letzterer Wert immer grösser ist als der Theorie entspricht, ist verständlich, denn die Reaktion muss bis zu einem gewissen Punkt fortschreiten, der es uns erlaubt sie wahrzunehmen. Es scheint also, dass im Grossen und Ganzen das Massenwirkungsgesetz genügt, um den Gang solcher Reaktionen — auf der Tüpfelplatte und in wenigen Sekunden Ausführungszeit — zu bestimmen.

Die obengenannten Tabellen weisen aber auch verschiedene Abweichungen auf. Das heisst: die Reaktion tritt auf, selbst wenn [D*] kleiner ist als die Beziehung (e) verlangt. Bei längerer Reaktionsdauer und vollkommener Vermischung der Suspension als auf der Tüpfelplatte möglich ist, treten diese „Abweichungen" in den meisten Systemen auf. Diese Tatsache könnte auf zumindest zwei Arten erklärt werden:

1. Hydrolytische Adsorption. Nach Tabelle II reagiert Calciumkarbonat mit geringeren Mengen Sulfat als durch den berechneten Wert möglich erscheint. Es könnte sich in diesem und in ähnlichen Fällen um eine hydrolytische Adsorption[15] handeln. Das Gleichgewicht

$$\begin{array}{l} Na_2SO_4 + H_2O \rightleftharpoons NaOH + NaHSO_4 \\ \hphantom{Na_2SO_4 + H_2O \rightleftharpoons NaOH + NaH} + \\ \hphantom{Na_2SO_4 + H_2O \rightleftharpoons NaOH +} H_2O \rightleftharpoons NaOH + H_2SO_4, \end{array}$$

das sich normalerweise nur unmerkbar von links nach rechts verlegt, würde in diesem Falle durch die vorzugsweise Adsorption der Schwefelsäure durch das Calciumkarbonat begünstigt. Dies hätte die alkalische Reaktion der Mischung zur Folge.

2. Austausch-Adsorption. Wenn man einen wenig löslichen Elektrolyten mit Wasser in Berührung bringt, bildet sich um die festen Partikel ein flüssiger Film, der schnell im Bezug auf die Ionen des festen Körpers gesättigt wird[14]. Wenn das Wasser einen anderen Elektrolyten in Lösung hat, diffundieren die Ionen dieses Elektrolyten in den flüssigen Film, da sie von den residuellen Valenzen der Oberflächenionen des Kristallgitters des festen Körpers angezogen werden. Die Ionenkonzentration kann deshalb im flüssigen Film, der die festen Teilchen umgibt, viel grösser sein als im restlichen Lösungsvolumen[24].

Auf Grund dieser in der Literatur dokumentierten Tatsachen scheint es glaubhaft, dass, selbst wenn die Totalkonzentration eines Ions in Lösung kleiner wäre, als die Minimalkonzentration, die nach Gleichung (e) zur Massenfällung notwendig ist, die Konzentrationsbedingungen in diesem flüssigen Film befriedigt sein könnten. Die Reaktion würde also im flüssigen Film, der die festen Teilchen umgibt, beginnen und als topochemischer Vorgang klassifiziert werden. Dass es sich wirklich um einen topochemischen Vorgang handelt, kann mit Leichtigkeit in vielen der beschriebenen Reaktionen beobachtet werden. Bereicherung des flüssigen Filmes und Fällung würden sich solange fortsetzen, bis die Lösung so

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arm geworden ist, dass die Menge der diffundierenden Ionen nicht mehr genügt um das Löslichkeitsprodukt zu erreichen. In dieser Weise käme es zu einem Gleichgewicht.

3. Diese Hypothese liefert eine Erklärung für die allgemein anerkannte Tatsache[37], dass ein ungefährer Parallelismus zwischen hoher Adsorption und kleiner Löslichkeit besteht. Dieser Parallelismus ist nur deshalb nicht vollkommen, weil andere Faktoren, wie Radius, Hydratation und Deformation der Ionen[16,36], in dem Vorgange der Adsorption (Diffusion der Ionen des löslichen Elektrolyten ins Innere des flüssigen Films) eine Rolle spielen.

Der für den analytischen Chemiker äusserst wichtige Vorgang der Kopräzipitation könnte auch durch obige Hypothese erklärt werden, denn es besteht eine grosse Analogie zwischen der Einschliessung von verunreinigenden Ionen in einem Niederschlag während seiner Fällung und den in vorliegender Mitteilung behandelten metathetischen Reaktionen.

4. Ganz andere Erklärungen der Tatsache, dass Ionenaustausch möglich ist, selbst wenn die Bedingungen für Massenfällung nicht erfüllt sind, wurden in der Literatur gegeben[21, 22, 23, 25]. Die nähere Prüfung der veröffentlichten Versuche zeigt aber den grossen Einfluss den das Löslichkeitsprodukt auf ihr Ergebniss ausübt. Dies lässt annehmen, dass die Vorgänge doch irgendwie vom Massenwirkungsgesetze abhängig sind.

Gegen einen vollkommen an Adsorption gebundenen Vorgang spricht auch, dass es sich nicht um die Affinität eines bestimmten Adsorbents für ein gewisses Ion handelt. Es geht um einen allgemeinen Vorgang, der zwischen irgendeinem wenig löslichen Elektrolyten und einem Ion in Lösung vonstatten geht, falls die Löslichkeitsbedingungen erfüllt sind.

5. Die im theoretischen Teil angegebene Gleichung (e) erlaubt die Durchführbarkeit einer grossen Zahl von Reaktionen vorauszusehen, die wahrscheinlich noch nicht beschrieben wurden. So kommen, zum Beispiel, im Werke JACOBSON's, „Encyclopedia of Chemical Reactions"[19], folgende Reaktionen, die alle in vorliegender Arbeit durchgeführt wurden, nicht vor:

$$\begin{array}{lllllllll}
CaCO_3 & + & 2F^- & \rightleftharpoons & CaF_2 & + & CO_3^{-2} \\
CaCO_3 & + & 2JO_3^- & \rightleftharpoons & Ca(JO_3)_2 & + & CO_3^{-2} \\
CaCO_3 & + & 2BrO_3^- & \rightleftharpoons & Ca(BrO_3)_2 & + & CO_3^{-2} \\
CaCO_3 & + & C_2O_4^{-2} & \rightleftharpoons & CaC_2O_4 & + & CO_3^{-2} \\
BaCO_3 & + & 2JO_3^- & \rightleftharpoons & Ba(JO_3)_2 & + & CO_3^{-2} \\
BaCO_3 & + & 2BrO_3^- & \rightleftharpoons & Ba(BrO_3)_2 & + & CO_3^{-2} \\
BaCO_3 & + & C_2O_4^{-2} & \rightleftharpoons & BaC_2O_4 & + & CO_3^{-2} \\
3BaCO_3 & + & 2PO_4^{-3} & \rightleftharpoons & Ba_3(PO_4)_2 & + & 3CO_3^{-2} \\
PbCO_3 & + & 2J^- & \rightleftharpoons & PbJ_2 & + & CO_3^{-2} \\
PbCO_3 & + & 2JO_3^- & \rightleftharpoons & Pb(JO_3)_2 & + & CO_3^{-2} \\
PbCO_3 & + & CrO_4^{-2} & \rightleftharpoons & PbCrO_4 & + & CO_3^{-2}
\end{array}$$

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$$\begin{array}{llllllll}
PbCO_3 & + & C_2O_4^{-2} & \rightleftharpoons & PbC_2O_4 & + & CO_3^{-2} \\
3PbCO_3 & + & 2PO_4^{-3} & \rightleftharpoons & Pb_3(PO_4)_2 & + & 3CO_3^{-2} \\
Pb(JO_3)_2 & + & CrO_4^{-2} & \rightleftharpoons & PbCrO_4 & + & 2JO_3^{-} \\
Pb(JO_3)_2 & + & SO_4^{-2} & \rightleftharpoons & PbSO_4 & + & 2JO_3^{-} \\
Pb(JO_3)_2 & + & C_2O_4^{-2} & \rightleftharpoons & PbC_2O_4 & + & 2JO_3^{-} \\
3Pb(JO_3)_2 & + & 2PO_4^{-3} & \rightleftharpoons & Pb_3(PO_4)_2 & + & 6JO_3^{-} \\
3Pb(JO_3)_2 & + & 2AsO_4^{-3} & \rightleftharpoons & Pb_3(AsO_4)_2 & + & 6JO_3^{-}
\end{array}$$

ERGEBNISSE

Die analytische Auswertung von Austauschreaktionen zwischen löslichen und wenig löslichen Elektrolyten ist interessant, da 1. ihre Ausführung sehr einfach ist; 2. sie die Umwandlung von Ionen für die es nur komplizierte, zweifelhafte oder wenig empfindliche Reaktionen gibt in andere, deren Identifizierung leichter, selektiver oder empfindlicher ist, ermöglichen; und 3. sie das Entwerfen von spezifischen oder selektiven Identitätsprüfungen durch Musterung der Tabelle der Löslichkeitsprodukte und der Ausführung einer einfachen auf dem Massenwirkungsgesetze begründeten Rechnung erlauben.

Die Beschränkungen dieser Art von analytischen Proben sind aber zahlreich. Die Reaktionen sind meist nicht vollständig; die Interferenz von vielen Ionen kann nur umgangen werden, indem man ihre Konzentration unter einer gewissen Grenze hält, die für jeden Fall eigens bestimmt werden muss; die Totalkonzentration selbst indifferenter Ionen in der Lösung darf nicht hoch sein; sekundäre Vorgänge, wie hydrolytische und Austausch-Adsorption, müssen oft in Erwägung gezogen werden. Ausserdem müssen die Angaben jedes Verfahrens ziemlich genau befolgt werden, um ähnliche Resultate zu erhalten. Daher sind die behandelten Austauschreaktionen endgültiger, wenn sie ein negatives Ergebniss zeigen, als im anderen Falle.

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An dieser Stelle sei Herrn DAVID GOLDSTEIN, Chemiker des Laboratório da Produção Mineral, Rio de Janeiro, für die konstruktive Diskussion, die der Verfasser mit ihm über viele Punkte der vorliegenden Mitteilung unterhalten durfte, herzlich gedankt.

ZUSAMMENFASSUNG

Nach der Besprechung der theoretischen Grundlagen von Austauschreaktionen zwischen löslichen und wenig löslichen Elektrolyten wurden ihre Vor- und Nachteile als analytische Proben durch folgende Beispiele veranschaulicht: 1. der Nachweis von Oxalat und Fluorid durch die Reaktion dieser Ionen mit Calciumkarbonat, 2. idem Sulfat und Chromat mit Bariumkarbonat, 3. idem Phosphat und Chromat mit Bleikarbonat, 4. idem die Halogene mit Silberkarbonat, 5. idem Bromid und Jodid mit Silberrhodanid, 6. idem Bromid mit Silberrhodanid und Belichtung, 7. idem Phosphat und Oxalat mit Bleijodat, 8. idem die Halogene mit Silberjodat.

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Der Mechanismus dieser Art von Reaktionen wurde erörtert und eine Hypothese aufgestellt, um zu erläutern, warum Ionenaustausch erfolgt, selbst wenn die Konzentration der Reagenzien geringer ist als für eine Massenfällung nötig wäre.

Viele der beschriebenen Reaktionen werden im Werke von JACOBSON, Encyclopedia of Chemical Reactions, nicht angegeben.

SUMMARY

After an explanation of the theoretical basis of exchange reactions between soluble and difficultly soluble electrolytes, their advantages and disadvantages as analytical test reactions were illustrated by the following examples:

1. identification of oxalate and fluoride by their reaction with calcium carbonate;
2. identification of sulfate and chromate with barium carbonate;
3. identification of phosphate and chromate with lead carbonate;
4. identification of the halogens with silver carbonate;
5. identification of bromide and iodide with silver thiocyanate;
6. identification of bromide with silver thiocyanate and photodecomposition;
7. identification of phosphate and oxalate with lead iodate;
8. identification of the halogens with silver iodate.

The mechanism of these reactions is discussed and a hypothesis formulated to explain why ion exchange ensues, even if the concentration of the reagents is smaller than would be necessary for mass precipitation. Many of the reactions described are not listed in JACOBSON's Encyclopedia of Chemical Reactions.

RÉSUMÉ

Après l'exposé des bases théoriques des réactions de double décomposition entre électrolytes solubles et peu solubles, l'auteur illustre les avantages et inconvénients de ces réactions du point de vue analytique par les exemples suivants:

1. identification des ions oxalique et fluorhydrique par la réaction au carbonate de calcium;
2. identification des ions sulfurique et chromique par le carbonate de baryum;
3. identification des ions phosphorique et chromique par le carbonate de plomb;
4. identification des ions halogénhydriques par le carbonate d'argent;
5. identification des ions bromhydrique et iodhydrique par le thiocyanate d'argent;
6. identification de l'ion bromhydrique par le thiocyanate d'argent et exposition à la lumière;
7. identification des ions phosphorique et oxalique par l'iodate de plomb;
8. identification des ions halogénhydriques par l'iodate d'argent.

Puis on discute le mécanisme de ces réactions et on énonce une hypothèse pour expliquer cet échange d'ions, même lorsque la concentration des réactifs est inférieure à celle exigée par la loi d'action de masses. Un grand nombre des réactions décrites ne sont pas données dans l'ouvrage de JACOBSON: Encyclopedia of Chemical Reactions.

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RAPIDANALYSE; ZEIT- UND MATERIAL-SPARENDE HALBAUTOMATISCHE VERDÜNNUNGSMETHODEN

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Das international vorherrschende Verfahren zur Verdünnung von Lösungen besteht in der Abtrennung eines bestimmten Volume und der Auffüllung zur Marke in einem Messkolben. Dabei werden also zehn ml zu neunzig oder zwanzig zu achtzig, oder mathematisch ausgedrückt N ml zu 100-N ml zugesetzt. Dies Verfahren erfordert verhältnismässig grosse Mengen an Flüssigkeit, denn kleine Maaskolben gibt es nicht oder sie sind sehr unhandlich, obendrein muss man *zwei* genaue Messoperationen vornehmen. Wir haben deshalb bei der Entwicklung der Technik unserer Rapidanalyse diese Methode verlassen und so weit als möglich durch diejenige *des Zusatzes konstanter Volumina zu einem variablen Volumen ersetzt.* Sowohl das konstante Volumen, als auch die variablen Volumina können gross oder beliebig klein gehalten werden, da man sie in letzterem Fall mit Pipetten oder Mikrobüretten abmisst. Man kann also nach Belieben von einem Liter oder einem Kubikzentimeter ausgehen. Das konstante Volumen kann automatisch zugesetzt werden, wodurch persönliche Fehler weitgehend ausgeschaltet werden. Dazu kommt, dass die Pipetten dauernd im Reagens verbleiben können, was eine beträchtliche Zeitersparnis bedeutet, da nur noch sehr wenige Pipetten gereinigt zu werden brauchen. Bei dem neuen Verfahren setzt man nicht mehr N zu 100-N, sondern X zu 100 ml zu. Also 1.11 ml zu zehn statt 1.0 ml zu neun usw. Es bleibt nur noch übrig festzustellen wie gross X in jedem Falle sein muss um die gewünschte Verdünnung zu erreichen und die Anwendungsmöglichkeiten zu beschreiben. X bedeutet die Menge, die man zu hundert ml Flüssigkeit (ev. Wasser) zusetzen muss um eine N% Lösung zu erhalten.

Berechnung der Wassermenge die man zusetzen muss um eine N% Verdünnung herzustellen.

Eine N% Lösung enthält 100-N Teile Wasser, X sei die gesuchte Wassermenge, dann ergibt sich die Proportion:

$N : 100\text{-}N = 100 : X$ und daraus

$$X = 100 \frac{(100\text{-}N)}{N} \text{ oder vereinfacht } 100 \left(\frac{100}{N} - 1\right)$$

Den Wert $\frac{100}{N}$ findet man in Tabellenwerken und Handbüchern wie Langes Handbook of Chemistry wo $\frac{1000}{N}$ angegeben ist.

Wir geben nachstehend die ganze Tabelle bis zu *N* gleich 50 also 50% an. Man kann sie auf einen Karton kopieren, denn sie hat zahlreiche Anwendungsmöglichkeiten.

N %	Zusatz zu 100 ml	50 ml	N %		
100			75	33.33	16.66
99	1.01	0.50	74	35.14	17.57
98	2.04	1.02	73	36.99	18.48
97	3.09	1.54	72	38.89	19.44
96	4.17	2.08	71	40.85	20.42
95	5.26	2.63	70	42.86	21.43
94	6.38	3.19	69	44.93	22.46
93	7.53	3.86	68	47.06	23.53
92	8.70	4.35	67	49.25	24.62
91	9.89	4.94	66	51.52	25.76
90	11.11	5.55	65	53.85	26.92
89	12.36	6.18	64	56.25	28.12
88	13.64	6.82	63	58.73	29.36
87	14.94	7.47	62	61.29	30.64
86	16.28	8.14	61	63.93	31.96
85	17.65	8.82	60	66.67	33.33
84	19.05	9.02	59	69.49	38.74
83	20.48	10.24	58	72.41	36.20
82	21.95	10.47	57	75.44	37.72
81	23.46	11.73	56	78.57	39.28
80	25.00	12.50	55	81.82	40.91
79	26.58	13.29	54	85.19	42.59
78	28.21	14.10	53	88.68	44.34
77	29.87	14.94	52	92.31	46.15
76	31.58	15.79	51	96.08	48.04
			50	100.00	50.00

Praktische Beispiele: *N* sei 80, man will also eine 80% Verdünnung herstellen. Die Tabelle zeigt $\frac{100}{80}$ gleich 1.25. Daraus ergibt sich als Endresultat (1.25-1.00) x 100 gleich 25.00. Der Wert in der Klammer bezeichnet also wieviel Wasser man zu einem Kubikzentimeter zusetzen müsste und das Resultat mit hundert multipliziert ist die Menge, die man zu hundert ml zusetzen muss um die 80% Lösung herzustellen. Sobald man Lösungen noch geringerer Konzentration als 50% herstellen will, kann man eben so weiter verfahren. Einfacher ist es aber dieselbe Tabelle zu benutzen, wobei aber die Werte, die vorher für die Lösung galten, jetzt auf das Wasser angewandt werden. Also 25 ml Losung zu 100 ml Wasser ergeben eine 20% Lösung, während vorher eine 80% erhalten wurde. Nach der Formel hätten wir 400 ml Wasser zu 100 ml Lösung zusetzen müssen, was unbequem viel ist.

Tabelle zur Herstellung von Verdünnungen durch Zusatz variabler Mengen zu 100 bzw. 50 ml Wasser ist auf vorhergehender Seite gegeben worden.

Die benötigte Menge ist $\left(\frac{100}{N} - 1\right)$ mal 100 resp. mal 50.

Durch Zusatz von 100 ml Wasser zu 100 ml Lösung bzw. von 50 zu 50, stellt man eine 50% Verdünnung her, fügt man 11.11 ml Wasser zu 100 ml Lösung so beträgt die Verdünnung 90% der Stammlösung usw.

Will man aber nur zehn oder gar fünf ml der Verdünnung herstellen, so nimmt man hundertmal weniger. Also 0.25 ml Stammlösung zu 1.0 ml Wasser ergeben eine Verdünnung, die 80% der Stammlösung enthält. Das alte Verfahren der Auffüllung zur Marke ist mit so kleinen Mengen gar nicht durchführbar und mit Pipetten recht umständlich auszuführen.

Um Stammlösungen auf einen Gehalt von weniger als 50% herabzusetzen, verfährt man wie folgt: Man setzt 0.25 Stammlösung zu 1.00 Wasser an, um eine 20% Stammlösung herzustellen. Was vorher an Stammlösung genommen wurde, verwendet man jetzt an Wasser und umgekehrt.

Praktische Anwendungsmöglichkeiten

Diese sind natürlich das Wichtigste und auf den ersten Blick nicht ohne weiteres zu erkennen. Auch wir haben Jahre gebraucht bis uns klar wurde, wo überall die neuen Verdünnungsmethoden mit Vorteil anwendbar sind oder gar neue Wege eröffnen. Seit mehreren Jahren benutzen wir die semi-automatischen Eiweissfällungsmethoden und erst in letzter Zeit erkannten wir die Anwendungsmöglichkeit bei der Photometrie und der Herstellung verdünnter Lösungen. Nachstehend einige Beispiele.

1) Herstellung verdünnter Lösungen, wenn nur wenig Material vorhanden ist oder in Arbeit genommen werden soll.

Dazu gehört die Herstellung verdünnter Lösungen aus konzentrierten Lösungen organischer oder anorganischer Art, z.B. 3% Salzlösung aus 10% für Meinicke Antigen, Glukoselösung, Verdünnungen zur Kontrolle des Eichwertes des Photometers von 1, 2, 3 oder mehr Einheiten, Ammoniakvergleichslösungen, etc. Die 3% Salzlösung bereitet man durch Zusatz von 4.28 ml der 10% Salzlösung zu 10 ml Wasser oder 23.2 Wasser zu 10 ml Salzlösung. Beide Operationen können automatisch ausgeführt werden mit Pipetten, die dauernd in der Lösung sind und nicht gewaschen zu werden brauchen. Die hergestellte Menge langt für 12 Analysen.

2) Herstellung verdünnter Serien.

Mitunter handelt es sich um Serien, die um 0.2 auseinanderliegen müssen, z.B. Kochsalzlösungen zur Blutkörperchenresistenzbestimmung. Das Zählen der Tropfen führt sicher zu Fehlern, wenn man bis zu 600 Tropfen zählen muss.

Eine Variation davon ist die Herstellung einer Lösung von geringerem Prozentgehalt aus einer stärkeren, z.B. Herstellung einer Lösung von 2.4% aus einer solchen die 7% stark ist. Diese Lösung hat eine Konzentration von 34.3% der stärkeren, denn 2.4 durch 7 dividiert mal 100 ergibt diesen Wert. Die Tabelle zeigt, dass der Zusatz von 5.38 ml der 7% Lösung zu 10 ml Wasser eine Verdünnung von 35% ergibt. Für die 34% braucht man 5.12 und will man den genauen Zwischenwert, so errechnet man ihn oder erweitert unsere Tabelle. Der Wert ist genau $\left(\frac{100}{65.7} - 1\right)$ 100 gleich 5.24 ml. Nimmt also soviel an starker Lösung und 10 ml an Wasser so erhält man eine 2.4% Lösung. Nimmt man aber umgekehrt 5.24 ml Wasser und 10 ml starker Lösung, so hat diese 65.7% der starken Lösung also etwa 4.6%.

3) *Halbautomatische Verdünnung mit gleichzeitiger Ausfällung*

Diese Methode ist bei den Millionen von Blutanalysen vorteilhaft anwendbar, gleichgültig, ob man dabei mit Wolframat-Schwefelsäure oder Zinksulfat Natronlauge oder anderen Fällungsmitteln enteiweisst. Man setzt automatisch zu 1.11 ml Blut je 5.0 ml von jedem der Fällungsmittel zu. Will man zwanzigmal verdünnen, so benutzt man 0.526 ml Blut auf je 5 ml Reagens A und B. Beide Reagenzien werden fünfmal verdünnter gebraucht als bei dem klassischen Verfahren, also 2% und 2/15 normal gegen 10% und 2/3 normal etc.

4) *Herstellung verdünnter Serien aus einer dunklen Lösung die zur Kalibrierung von Photometern dienen soll*

Wie wir anderen Orts genauer darlegen wollen, genügt eine einzige Röhrchenfüllung von z.B. nur 5 ml um alle beliebigen Zwischenverdünnungen durch succesiven Zusatz von Lösungsmittel herzustellen. Die einfachste Kalibrierung für sämtliche pH Werte ist so mit einer Indikatorlösung beliebiger Konzentration durchzuführen. Die Verdünnung auf das Doppelte zeigt die Halbwertsstufe an und alle Zwischenwerte entsprechen Zwischenfarben. Es sind dabei keine Pufferlösungen erforderlich.

5) *Halbautomatische Herstellung von Standardlösungen*

Hier handelt es sich nicht um Verdünnung einer Flüssigkeit, sondern so zu sagen um die eines festen Körpers. Durch einfaches Übergiessen der abgewogenen Salzmenge mit 1000 ml Wasser erhält man so die Standardlösung. Ein Messkolben bei dem der Stopfen den Inhalt begrenzt, erlaubt die automatische Abmessung des richtigen Volumens ohne Meniskusfehler.

Das hier abgebildete Modell wurde uns von der Firma Emil Greiner in New York hergestellt und besteht aus einem Messkolben mit eingeschliffenem Stopfen, der aber statt der zentralen Bohrung zwei Seitenkanäle hat. Der Kolben kann nach Art eines Pyknometers benutzt werden, aber auch in alter Art mit Auffüllung bis oben. Die neue Methode erlaubt es, die Standardlösungen direkt im Vorratsgefäss anzusetzen. Der Messkolben wird dabei mit einer geringen Menge der Standardlösung nachgespült, so dass er auf Einguss geeicht werden muss. Die abzuwiegende Menge muss natürlich ein für alle Mal aus dem spezifischen Gewicht der fertigen Normallösungen berechnet werden.

Wir wollen hier bemerken, dass die auf dem amerikanischen Markt angebotenen automatischen Pipetten mit Gummiball, sicherlich vorzüglich zu gebrauchen wären. Dazu käme eine Mikroburette, um alle variablen Verdünnungen mit fünf ml Lösung vornehmen zu können. Der Mangel an Devisen und unsere Finanzlage haben es uns nie gestattet diese Dinge praktisch zu benutzen. Zahlreiche Chemiker in der ganzen Welt sind aber in unserer Lage und daher geben wir hier das einfachste System das überall benutzbar ist. Muss stets die gleiche Menge entnommen werden, so lässt man einfach dauernd eine Pipette im Reagens stecken und überdeckt deren Öffnung mit einem umgestülpten Reagensglas. Mikrobüretten stellt man sich aus graduierten Pipetten selbst her indem man sie in einem Stativ befestigt und oben mit einer Ansaugvorrichtung versieht. Diese gibt es im Handel, aber man kann sie sich selbst aus einem Quetschhahn mit Gummiball herstellen. Der Quetschhahn vom Hoffmanschen Typ, wie er für Gasschläuche benutzt wird, ist vorzüglich, da die Schraube eine Feineinstellung gestattet. Wir halten diese Mikrobüretten für besser, als die mit Glashahn wie sie für die Hagedorn-Jensen-Titrationen benutzt werden. Sie sind leicht zu füllen, leicht zu reinigen und sehr billig, obendrein kann man zu grosse Tropfen wieder zurücksaugen, was sonst nicht möglich ist.

6) *Vollautomatische Ausführung klinischer und mancher technischer Analysen*

Eine Kombination der Abmessungs- und Verdünnungsmethoden, auf deren Einzelheiten wir hier nicht eingehen können, erlaubt es zahlreiche Bestimmungen in praktisch vollautomatischer Weise auszuführen. Nur die Operation des Abmessens oder des Abwiegens des Untersuchungs- und ev. des Vergleichmaterials verlangt Aufmerksamkeit. Alles Übrige erledigt sich durch automatische Entnahme oder Zusatz der Reagenzienlösungen und ev. Filtrate. Eine Ausrechnung der Resultate erübrigt sich, da diese aus einer Tabelle entnommen werden können. Beispiel: Blutzucker. Vom Eiweisfiltrat entnimmt man 2 ml setzt 2 ml Reagens C zu, kocht sieben Minuten, setzt 2 ml Reagens D zu, setzt automatisch bis zu 25 ml Wasser zu und entnimmt den Wert aus der Photometertabelle oder durch Vergleich mit dem ebenso behandelten Glukoseeichwert. Man könnte genau so gut Nitrite, Metalle etc. bestimmen, so lange keine komplizierten Zwischenoperationen erforderlich sind.

Unsere Technik verlangt daher nur noch selten speziell vorgebildetes Personal zur Ausführung von Analysen und ermöglicht es im besonderen dem praktischen Arzt, alle Patienten analytisch selbst zu betreuen.

ZUSAMMENFASSUNG

Die Methoden des Zusatzes variabler Volumina von Flüssigkeiten zu einem konstanten Volumen erlauben es, schnell, genau und oft in fast automatischer Weise zu arbeiten. Sie können erfolgreich zur Herstellung verdünnter Lösungen, zur Kalibration von Photometern, zur automatischen Enteiweissung von Blut und selbst zur Herstellung von Normallösungen gebraucht werden. Dies ist besonders interessant für Kliniken, da die meisten Analysen so von Personal ohne jede technische Vorbildung ausgeführt werden kann. Die gleiche Vorzüge gelten aber auch für viele technische Analysen.

SUMMARY

Dilution methods based on the principle of the addition of variable volumes to a constant volume of liquid are described. They are fast, accurate and frequently half or completely automatic. They may be applied successfully to the preparation of diluted solutions, calibration of photometers, automatic deproteinization of blood samples and even to the preparation of standard solutions. In the clinical field, with the help of these methods, most analyses can be performed by completely untrained personnel. The same advantages hold good for many technical determinations.

RÉSUMÉ

Des méthodes de dilution, consistant à ajouter des volumes variables à un volume constant de solution, sont décrites. Elles peuvent être appliquées avec succès à la préparation de solutions diluées, au calibrage de photomètre, à la déprotéinisation du sang, et même à la préparation de solutions étalon. Dans le domaine médical, elles permettent de faire faire la plupart des analyses par un personnel non spécialisé. Il en est de même pour de nombreuses déterminations techniques.

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THE DETERMINATION OF LOW CONCENTRATIONS OF OXYGEN IN GASES BY THE MANGANOUS HYDROXIDE METHOD

by

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INTRODUCTION

As long ago as 1888 WINKLER[1] suggested the manganous hydroxide method for the determination of low concentrations of oxygen in water. In later years, the application of this principle to the determination of oxygen in gases has been discussed by a great many authors[2-11], of which we mention as the most recent ones: WINSLOW AND LIEBHAFSKY[8], MEYER AND GHIJSEN[9], TAYLOR AND ALEXANDER[11], and ASTM method D 1021-49 T[10].

Until recently there was no reliable reference method to verify the results obtained by means of the manganous hydroxide method. By introducing mass spectrometry this possibility has been created. Gas samples with an accurately known oxygen content, which has been determined with the aid of a mass spectrometer, can now serve as reference substances to test the method for chemical determination of oxygen.

TAYLOR AND ALEXANDER[11] did this with ASTM method D 1021-49T[10] and found that the results obtained when using this version of the manganous hydroxide method were too high at low oxygen concentrations ($< 0.5\%$ vol.) and too low at high oxygen concentrations ($< 0.5\%$ vol.). These authors suggest, therefore, that the experimental values should be corrected with the aid of a calibration curve.

Generally speaking, there are many objections to using a correction factor. Therefore, in the present investigation it has been ascertained whether the manganous hydroxide method can be carried out in such a way that the values obtained are correct also without using a correction factor.

On the strength of the experience gained in the course of several years with the version suggested by MEYER AND GHIJSEN[9] we are of opinion that the high values found by TAYLOR AND ALEXANDER[11] at oxygen concentrations below 0.5% vol. are to be attributed to the oxygen dissolved in the reagents. Indeed TAYLOR AND ALEXANDER require the use of oxygen-free solutions, but inevitably these solutions rapidly absorb oxygen from the air on being stored. For these reasons it is recommended to apply the method for deaeration of reagents suggested by Meyer and Ghijsen. According to this method the liquids in the reaction vessel, immediately before use, are rendered perfectly oxygen-free in vacuo and at a high temperature. The blank value is so low that it can be neglected, also when the gases to be measured have oxygen concentrations lower than 0.1% vol.

The reason why in the ASTM method as well as in the modification suggested by Taylor and Alexander too low values are found at oxygen concentrations of from 0.5 to 4% probably is the incomplete reaction between the oxygen and the reagents. Both the nature and concentration of the hydroxide precipitate and the reaction time play a part here.

The above-mentioned suppositions have been further ascertained and on the strength of the results obtained an improved procedure of the manganous hydroxide method has been formulated, which is described in detail in the Appendix. Using this procedure reliable values for oxygen contents below 4% vol. are obtained without applying a correction factor.

EXPERIMENTAL WORK

Briefly, the method is as follows:

In a glass vessel containing a dilute $MnCl_2$ solution there is a test tube containing alkaline KI solution. After deaeration of the vessel and the two reagents the gas to be analysed is admitted and the reagents are mixed. When the gas and the reagents have been in contact sufficiently long, hydrochloric acid is added and the iodine liberated is titrated with thiosulphate. The consumption of sulphate is a measure of the oxygen content of the gas.

Standard gas mixtures

To judge the method it is necessary to have a series of gas mixtures of known oxygen concentration. There is some difficulty in making large quantities of synthetic gas mixtures by combining known volumes of gas, however, as the gas of dilution must be completely free of O_2 and air must be completely eliminated.

TABLE I

MASS-SPECTROMETRIC ANALYSIS OF GAS MIXTURES

Gas sample No.	Oxygen concentration % vol.	Precision	
		% vol.	%
1	0.13	±0.01	±7.7
2	0.94	±0.02	±1.9
3	1.67	±0.02	±1.2
4	2.91	±0.03	±1.0
5	3.75	±0.03	±0.8

Therefore, some O_2/N_2 mixtures of roughly known composition were made in stainless steel bombs. After being left for some days to ensure complete homogenization, they were accurately analysed with the aid of a mass spectrometer. Results are recorded in Table I.

The oxygen contents found with the aid of the mass spectrometer will be referred to below as the "theoretical oxygen contents".

Variables in the manganous hydroxide method

For many years this Laboratory has used the procedure described by MEYER AND GHIJSEN[9], starting from a solution of manganous chloride saturated at room temperature and containing *ca* 800 g of the hydrate per litre. A quantity of 5 ml of this solution was used for every determination.

The standard gas samples nos. 1—5 were analysed according to the procedure of MEYER AND GHIJSEN, the results of which are listed in Table II.

TABLE II

OXYGEN DETERMINATION BY THE MEYER-GHIJSEN METHOD

Conditions: Shaking time : 1 hour
Vol. of saturated $MnCl_2$ solution: ml

Gas sample No.	"Theoretical oxygen", % vol.	Experimental oxygen % vol.	Average, % vol.	Deviation from the average, % vol.	Deviation of the average from "theoretical oxygen", % vol.
1	0.13	0.110	0.106	+0.004	—0.024
		0.101		—0.005	
		0.109		+0.003	
		0.103		—0.003	
2	0.94	0.714	0.722	—0.008	—0.22
		0.715		—0.007	
		0.733		+0.011	
		0.724		+0.002	
3	1.67	1.18	1.21	—0.03	—0.46
		1.20		—0.01	
		1.22		+0.01	
		1.24		+0.03	
4	2.91	2.30	2.44	—0.14	—0.47
		2.38		—0.06	
		2.67		+0.23	
		2.41		—0.03	
5	3.75	2.86	2.56	+0.30	—1.19
		2.25		—0.31	

It is apparent from these analyses that for all oxygen contents of from 0.1 to 3.75% by vol. the findings are considerably too low. In spite of the fact that the accuracy is poor, the results obtained from analyses of one sample show little spread, in other words, the reproducibility of the test is good. TAYLOR AND ALEXANDER[11] also observed this and drew up their correction on the basis of this fact.

The deviation of the average oxygen content of every sample from the theoretical value is greater according as the O_2 concentration is higher. This suggests a systematic error whose cause must a priori be sought in incomplete reaction of the reagent, in this case the manganous hydroxide, with the oxygen in the sample.

For these reasons it was tried in the first place to promote the reaction by prolonging the time of contact between reagents and oxygen. In continuation, the influence of the concentrations of these reagents was ascertained.

Shaking time

It is known that the oxidation of manganous hydroxide in an aqueous medium at room temperature is but slow, the nature of the hydroxide precipitate and its concentration in the liquid playing an important part. The precipitate is oxidized only at the surface, the resultant layer of oxide impeding further oxidation of the manganous hydroxide.

The progress of the oxidation reaction can thus be promoted by extending the contact time between the gas and the reagent, as is shown by the observations recorded in Table III.

TABLE III

OXYGEN DETERMINATION WITH LONGER SHAKING TIME

Conditions: Shaking time : 2 hours
Vol. of saturated $MnCl_2$ solution: 5 ml

Gas sample No.	"Theoretical oxygen", % vol.	Experimental oxygen, % vol.	Average, % vol.	Deviation from the average % vol.	Deviation of average from "theoretical oxygen", % vol.
2	0.94	0.88	0.85	+0.03	−0.09
		0.90		+0.05	
		0.81		−0.04	
		0.81		−0.04	
3	1.67	1.64	1.65	−0.01	−0.02
		1.66		+0.01	
4	2.91	2.74	2.74		−0.17
5	3.75	3.57	3.18	+0.39	−0.57
		2.70		−0.48	
		3.26		+0.08	

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The results obtained when allowing two hours' shaking time are considerably better. However, extending the shaking time is not an attractive means of improving the method as the total duration of the analysis then becomes too long.

Concentration of reagents

The influence of the nature and concentration of the manganous hydroxide was next studied. Originally, 5 ml of a saturated $MnCl_2.4H_2O$ solution (800 g/litre, *ca.* 20° C) was introduced into 100 ml of water. The solution then contains about 4 g of the salt, which, upon complete oxidation, can bind about 225 ml of oxygen. In a gas sample of about one litre, at a concentration of 4% by vol. of oxygen, there is only about 40 ml of oxygen. The excess of manganese ions is therefore very large. It was ascertained whether better results can be obtained at different manganese concentrations. See Table IV.

TABLE IV

OXYGEN DETERMINATION WITH DIFFERENT MANGANOUS HYDROXIDE CONCENTRATIONS

Conditions: Shaking time : 1 hour
Vol. of saturated $MnCl_2$ solution: see table

Gas sample No.	ml of $MnCl_2$ solution per 100 ml H_2O	"Theoretical oxygen", % vol.	Experimental oxygen, % vol.	Deviation from theoretical oxygen, % vol.
1	0.5	0.13	0.114	—0.016
	1		0.112	—0.018
	2		0.118	—0.012
	2		0.116	—0.014
	5		0.106	—0.024
2	1	0.94	0.912	—0.028
	1.5		0.922	—0.018
	2		0.944	+0.004
	2.5		0.949	+0.009
	3		0.955	+0.015
	4		0.630	—0.310
	5		0.722	—0.218
	1	3.75	3.61	—0.14
	2		3.71	—0.04
	2		3.83	+0.08
	3		3.68	—0.07
	5		2.56	—1.19
	10		3.30	—0.45

The best results are obtained when 2 ml * of saturated manganous chloride solution is added per 100 ml of water. It is noteworthy that at this concentration the precipitate formed is very finely distributed and there is much foaming. The consequent intimate contact between the gas and precipitate undoubtedly accounts for the more accurate results.

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* For practical purposes, 5 ml of a 30% $MnCl_2.4H_2O$ solution are used in the final procedure as given in the Appendix. This quantity equals the 2 ml of saturated manganous chloride solution referred to above.

The question then arose whether at this most favourable concentration a shorter contact time might be allowed. This is not the case, as will be seen from Table V.

TABLE V

OXYGEN DETERMINATION WITH VARIOUS SHAKING TIMES

Conditions: Shaking time : see table
Vol. of saturated $MnCl_2$ solution: 2 ml per 100 ml H_2O

Gas sample No.	Shaking time min.	"Theoretical oxygen", % vol.	Experimental oxygen, % vol.	Deviation from theoretical oxygen, % vol.
2	10	0.94	0.454	—0.486
	20		0.750	—0.190
	30		0.843	—0.097
	45		0.919	—0.021
	60		0.944	+0.004

A single experiment made with addition of a few drops of a surface-active agent solution in order to promote foaming showed that even under these conditions the shaking time of one hour cannot be reduced.

PRECISION

Oxygen concentrations of from 0.1 *to* 4.0% *vol.*

It is evident from the above that when 2 ml of saturated $MnCl_2$ solution in 100 ml of water is used and a shaking time of one hour is applied, the results are in good agreement with the mass-spectrometric analysis. For the sake of completeness some measurements were carried out under these conditions to ascertain the repeatability of this version of the manganous hydroxide method (see Appendix). The results are given in Table VI.

The normal distribution in the spread in results enables a standard deviation to be derived for any concentration. The standard deviation is proportionally the same for every measured concentration and is equal to:

$$s_X = 0.012\ X$$

in which X is the observed oxygen concentration.

The reproducibility of the determination can be 3.0 times the standard deviation as given by Student's "t" test (with 21-5 = 16 degrees of freedom) *i.e.* 0.036 X, or about 3.6% of the measured oxygen concentration.

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TABLE VI

OXYGEN DETERMINATION BY THE IMPROVED PROCEDURE

Conditions: Shaking time : 1 hour
Vol. of saturated $MnCl_2$ solution: 2 ml per 100 ml H_2O

Gas sample No.	"Theoretical oxygen", % vol.	Experimental oxygen, % vol.	Average experimental oxygen, % vol.	Standard deviation % vol.
1	0.13 ±0.01	0.115 0.115 0.116 0.118	0.116	0.001
2	0.94 ±0.02	0.944 0.941 0.949 0.955	0.947	0.011
3	1.67 ±0.02	1.69 1.70 1.71 1.72	1.71	0.02
4	2.91 ±0.03	2.96 2.96 2.97 3.00	2.97	0.03
5	3.75 ±0.03	3.68 3.71 3.73 3.79 3.83	3.75	0.04

Oxygen concentrations of less than 0.1% *vol.*

For very low oxygen concentrations there is no reliable method of comparison like the mass-spectrometric analysis referred to above, as this technique gives only reliable results at concentrations higher than 0.05%.

The results of the analyses of higher oxygen concentrations make it seem likely that correct results will also be found for the lowest concentrations by the improved manganous hydroxide method. Allowance should, however, be made for the increasing influence of any remnants of dissolved oxygen in the reagents and for the inaccuracy of the determination of the end-point of the titration.

Carefully carried out blank tests produced a minimum value corresponding to about 0.001% by vol. of oxygen. This value therefore gives the order of magnitude of the lowest oxygen concentration which can be estimated.

The standard deviation and reproducibility in the low concentration area can be determined from the measurements referred to in Table VII, carried out in nitrogen with a very low oxygen content.

TABLE VII

OXYGEN DETERMINATION IN LOW CONCENTRATIONS

Experimental oxygen, % vol. (x)	Deviation from average value, % vol, $(\bar{x}-x)\times 10^{-3}$	Square of deviation $(\bar{x}-x)^2\times 10^{-6}$
0.0139	1.7	2.89
0.0108	1.4	1.96
0.0108	1.4	1.96
0.0125	0.3	0.09
0.0138	1.7	2.56
0.0135	1.3	1.69
0.0123	0.1	0.01
0.0117	0.6	0.36
0.0106	1.6	2.56

Average value, $\bar{x} = \dfrac{0.1099}{9} = 0.0122.$

Sum of squares, $\Sigma\,(\bar{x} - x)^2 = 14.08 \times 10^{-6}$

Standard deviation, $s = \sqrt{\dfrac{\Sigma\,(\bar{x} - x)^2}{n - 1}} = \sqrt{\dfrac{14.08 \times 10^{-6}}{8}} = 0.0013\%$ vol.

Reproducibility (according to Student's "t" test, 8 degrees of freedom),
$= 3.3\,s = 3.3 \times 0.0013 = 0.004\%$ vol. O_2.

When comparing the standard deviations found for the determinations of oxygen concentrations higher and lower than 0.1% by vol. the following may be noted. It appears that, whereas at O_2 concentrations higher than 0.1% the standard deviation is a linear function of this concentration (e.g. 0.012 X, Table VI), at O_2 concentrations of less than 0.1% the standard deviation increases to a higher value which seems to be no longer a linear function of the oxygen concentration.

At the O_2 concentration of 0.1%, the standard deviation will be $0.012 \times 0.1 = 0.0012\%$ vol. This value is nearly the same as the standard deviation (0.0013%) found for oxygen concentrations averaging 0.0122% (see Table VII). From this fact we may derive that the standard deviation becomes a constant for all oxygen concentrations below 0.1% vol. This constancy is most probably due to the blank value of 0.001% vol.

Influence of various gases on the oxygen determination

It is not possible to determine oxygen in gases that react with the reagents. Reactions may then occur with the manganous hydroxide or the iodine.

Gases like hydrogen sulphide or hydrogen cyanide should be removed before the test, for instance by washing the sample with caustic solution. Carbon dioxide does not interfere with the test, nor do saturated hydrocarbons. The influence of unsaturated hydrocarbons was investigated: ethene and acetylene have no adverse effect, as was already shown by SZABÓ[12]; nor has butadiene.

SZABÓ reports, however, that carbon monoxide interferes with the test owing to its oxidation. Our measurements as recorded in Table VIII, carried out in comparison with mass-spectrometric analyses, do not confirm SZABÓ's statement.

TABLE VIII

OXYGEN DETERMINATION OF GASES CONTAINING CARBON MONOXIDE

Gas sample Description	No.	Carbon monoxide concentration, % vol.	"Theoretical oxygen", % vol.	Experimental oxygen, % vol.
Mixtures of synthesis gas and technical nitrogen	6	40.5	2.13	2.21
	7	0.6	0.23	0.26

The experimental values are both somewhat higher than the "theoretical" ones, but the difference is not significant. Furthermore, the deviation is the opposite of that mentioned by SZABÓ, There is therefore no question of any disturbing effect of carbon monoxide on this determination.

CONCLUSIONS

The investigation showed that the "manganous hydroxide method" for determining low oxygen concentration up to 4% by vol. can produce accurate results provided:

1. The reaction vessel and reagents are first thoroughly deaerated in vacuo at elevated temperature;
2. The $MnCl_2$ concentration of the solution is such as to produce a very finely distributed manganous hydroxide precipitate after it has been mixed with the alkaline KI solution. The most favourable $MnCl_2$ concentration was found to be 2 ml saturated solution in 100 ml water instead of the 5 ml used by MEYER AND GHIJSEN. An auxiliary factor is then moreover foaming, which enhances the contact with the gas;
3. The reaction time is sufficiently long (one hour).

If due allowance is made for these points no correction factor need be applied to the oxygen content experimentally found, in the way TAYLOR[11] does.

Neither unsaturated hydrocarbons, including acetylene, nor carbon monoxide interfere with the determination.

For oxygen concentrations of from 0.1 to 4% by volume the reproducibility is equal to 3.6% of the oxygen content.

With concentrations lower than 0.1% by vol. of oxygen the reproducibility is equal to 0.004% by vol. of oxygen.

APPENDIX

MANGANOUS HYDROXIDE METHOD FOR THE DETERMINATION OF LOW CONCENTRATIONS OF OXYGEN IN GASES

Method summary

A measured quantity of gas is shaken with a freshly prepared suspension of manganous hydroxide and potassium iodide in an aqueous medium. The manganous hydroxide is oxidized by the oxygen, an equivalent amount of iodine then being liberated upon treatment with hydrochloric acid. The iodine formed is titrated with standard sodium thiosulphate solution and the oxygen content calculated.

Apparatus

The apparatus is shown in Fig. 1 and consists of a *reaction pipette* of a special thick-walled type as illustrated in Fig. 2, and of a *manifold* fitted with a three-way

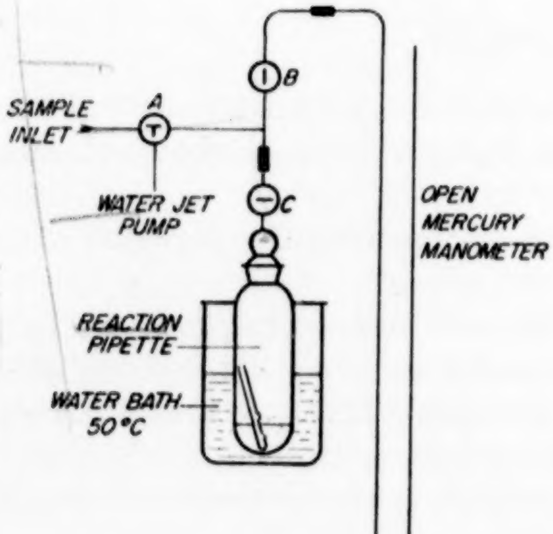

Fig. 1. Apparatus assembly

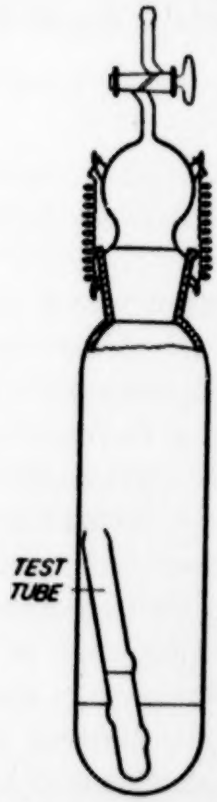

Fig. 2. 1 l reaction pipette

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stopcock, a normal stopcock and an open mercury type manometer. A *shaking machine* and a *vacuum device* capable of maintaining an absolute pressure of less than 25 mm of mercury complete the installation.

Reagents

Alkaline potassium iodide solution, containing 195 g of iodate-free KI and 390 g of c.p. KOH per litre.

Hydrochloric acid, 20%, made chlorine-free by boiling for 5 minutes.

Manganous chloride solution, 30% wt, 345 g of the tetrahydrate per litre.

Sodium thiosulphate solution, $0.1N$ and $0.01N$.

Starch indicator solution.

Water-insoluble lubricant, Apiezon M.

Procedure

Introduce 5 ml of manganous chloride solution, 100 ml of distilled water and some boiling chips into the pipette. Introduce 5 ml of the alkaline potassium iodide solution into a thin-walled test tube in which bumps are blown to increase fragility. Place the tube carefully in the pipette and connect the latter to the stopcock manifold. Place a water bath of about 50° C around the pipette and evacuate the apparatus by means of the vacuum pump.

Because of the very low pressure in the pipette the liquid will boil vigorously at 50° C. As a result of this boiling, all air is expelled from the reagent solutions and the apparatus. The danger that splashes of manganous chloride solution enter the test tube is eliminated by narrowing (not closing!) the opening of the test tube.

After a quarter of an hour close stopcock C and allow the pipette to cool down. Flush the manifold twice with the gas under test by alternately filling and evacuating.

Open stopcock C and fill the pipette with the gas under test. Evacuate again and refill with the gas sample to a pressure slightly below atmospheric, and record the pressure in the pipette.

Close stopcock C, disconnect the pipette from the manifold, dry and weigh the pipette to the nearest gram.

Shake the pipette vigorously for a moment in order to crush the test tube and to induce the formation of the manganous hydroxide suspension. Fill the inlet capillary of the stopcock with water as a check on leaking and provide with a rubber cap. Place the pipette in the shaking machine in a horizontal position, to obtain intimate contact between liquid and gas.

After one hour's shaking place a small glass funnel on the inlet capillary by means of a short piece of rubber tubing, pour in about 10 ml of 20% hydrochloric acid and remove all air from the capillary and funnel by "pumping" with a thin glass rod or capillary. Introduce the hydrochloric acid into the pipette preventing air from entering the pipette. Swirl the pipette until all precipitate is dissolved, remove the stopper, rinse the inside with distilled water, collecting the washings in the pipette and titrate the liberated iodine in the pipette with standard sodium thiosulphate solution using starch solution as indicator.

Fill the pipette provided with stopper completely with water and weigh to the nearest gram.

Calculate the oxygen content of the gas by means of the following equation:

$$\text{Oxygen, \% vol.} = \frac{A \times N \times 560}{V}$$

where:

A = volume of standard sodium thiosulphate solution used for titration, millilitres,

N = normality of the standard sodium thiosulphate solution and

V = volume of gas sample in millilitres of dry gas at standard temperature and pressure.

ACKNOWLEDGEMENTS

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SUMMARY

The present article describes an investigation into the manganous hydroxide method for determining low concentrations of oxygen in gases. It is shown that deaeration of the reagents in vacuo at elevated temperatures, the concentration of the manganous hydroxide, which has to be such as to produce a finely distributed precipitate, and the reaction time are the factors that determine the correctness of the analysis. Neither unsaturated hydrocarbons, including acetylene, nor carbon monoxide interfere with the determination. For oxygen concentrations of from 0.1 to 4% by volume, the reproducibility is equal to 3.6% of the oxygen content. With concentrations lower than 0.1% by volume of oxygen, the reproducibility is equal to 0.004% by volume of oxygen. A detailed description of the method is given in the Appendix.

RÉSUMÉ

Cet article décrit une étude concernant la méthode à l'hydroxyde de manganèse pour le dosage de faibles quantités d'oxygène dans les gaz. On a démontré que la désaération dans le vide des réactifs à une température élevée, la concentration de l'hydroxyde de manganèse, qui doit être telle qu'un précipité finement divisé se produise, ainsi que la durée de la réaction sont les facteurs qui déterminent la précision des analyses. Ni les hydrocarbures non-saturés, y compris l'acétylène, ni l'oxyde de carbone ne gênent la détermination. Pour des teneurs en oxygène de 0.1 à 4% en volume la précision est égale à 3.6% de la teneur en oxygène. Pour des concentrations inférieures à 0.1% en volume la précision équivaut 0.004% en volume d'oxygène. Une description détaillée de la méthode est donnée en appendice.

ZUSAMMENFASSUNG

Dieser Artikel beschreibt eine Untersuchung der Manganhydroxyd-Methode für die Bestimmung niedriger Sauerstoffkonzentrationen in Gasen. Es wird gezeigt, dass Entlüftung der Reagenzien im Vakuum bei höheren Temperaturen, die Mangan-(II)-hydroxydkonzentration — die einen solchen Wert haben soll, dass ein feinverteiltes Prezipitat entsteht — und die Reaktionszeit die Faktore sind, die zur Richtigkeit der Analyse beitragen. Weder ungesättigte Kohlenwasserstoffe, Azetylen mit einbegriffen, noch Kohlenmonoxyd stören die Bestimmung. Für Sauerstoffkonzentrationen von 0.1 bis 4 Vol. % ist die Bestimmung innerhalb 3.6% des Sauerstoffgehaltes reproduzierbar. Bei niedrigeren Konzentrationen als 0.1 Vol. % ist die Bestimmung innerhalb 0.004 Vol. % Sauerstoff reproduzierbar.

Eine ausführliche Beschreibung des Verfahrens wird im ,,Appendix" gegeben.

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EXTRACTION OF CATIONS AS SALTS OF FATTY ACIDS
II. ANALYTICAL AND CHROMATOGRAPHIC SEPARATION OF BERYLLIUM FROM IRON AND ALUMINIUM

by

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The conditions for the extraction of beryllium in the presence of butyric acid have already been reported[1,2]. This note deals with a similar study of the conditions for the extraction of iron and aluminium and the application of this method to the separation of beryllium from iron and aluminium. The experimental procedure adopted for these studies is identical with that already described for beryllium[2]. Chloroform, ethyl acetate, carbon tetrachloride and benzene were tried as solvents, but nearly complete extraction was obtained only with the first two. Chloroform was finally chosen as solvent because beryllium is more completely extracted in this solvent. Tables I and II indicate briefly the results obtained with iron and aluminium.

As the conditions for the extraction of beryllium, iron and aluminium in presence of butyric acid with chloroform are very much the same, separation was effected by the addition of complexon II (sodium salt of ethylenediamine-tetra-acetic acid) prior to the addition of butyric acid. Beryllium is extracted in organic phase whereas aluminium remains in water phase.

Tables III and IV give the results obtained on the separation of the beryllium from iron and aluminium, respectively. Table V contains the results of the separation of beryllium from synthetic mixture containing beryllium, iron and aluminium equivalent to 29 mg BeO, 19.4 mg Fe_2O_3 and 29.7 mg Al_2O_3 using complexon II, butyric acid and chloroform.

This method has also been tried on standard samples of beryl ore and found to be in excellent agreement with the known values of BeO contents.

Separation of beryllium from iron and aluminium is effected by eluting with 5% solution of butyric acid in ethyl acetate on the paper pulp column as efficiently as it does by extracting with chloroform in a separating funnel.

Chloride, nitrate, sulphate, silicic acid, magnesium, zirconium, titanium and small amounts of fluoride do not interfere. Phosphate, however, causes serious interference. The interference of phosphate up to 4 mg P_2O_5 is avoided by adding zirconyl chloride to the mixture and then adding sufficient complexon II to complex the excess of zirconium present.

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Further studies on the extraction of cations as salts of fatty acids are in progress and a full report will be published shortly.

TABLE I

Amount of iron for extraction: 19.7 mg as Fe_2O_3
Solvent: 50 ml of chloroform

pH of solution before addition of butyric acid	Volume of butyric acid in ml	pH of the solution after addition of butyric acid	Remarks
9.0	5	3.25	Incomplete extraction
9.5	5	3.80	-do-
10.0	5	4.20	Complete extraction
10.0	10	3.90	-do-
10.5	10	4.00	-do-

TABLE II

Amount of aluminium for extraction: 29.7 mg of Al_2O_3
Solvent: 50 ml of chloroform

pH of solution before addition of butyric acid	Volume of butyric acid in ml	pH of the solution after addition of butyric acid	Remarks
8.5	15	3.10	Incomplete extraction
9.2	15	3.40	Complete extraction
9.7	25	3.75	-do-
9.7	30	3.70	-do-
10.0	45	3.85	-do-

Minimum amount required to dissolve the precipitate caused by adding NH_4OH.

TABLE III

Amount of beryllium: 29.0 mg of BeO
Amount of iron: 19.4 of Fe_2O_3
Complexon II (10% solution in NH_4OH) 2 ml
Potassium chloride saturated solution 10 ml
pH: 9.7*
Solvent: 50 ml of chloroform

Vol. of butyric acid in ml	pH of the solution after addition of butyric acid	No. of extractions	BeO in solvent layer in mg
15	4.10	1	27.3 ± 0.2
25	3.75	1	28.1 ± 0.2
25	3.75	2	29.0 ± 0.2

* Extraction of Be is maximum at pH = 9.7

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TABLE IV

Amount of beryllium:	29.0 mg of BeO
Amount of aluminium:	29.7 mg of Al_2O_3
Complexon (10% solution):	4 ml
Potassium chloride (saturated solution):	10 ml
pH:	9.7
Solvent:	50 ml of chloroform

No. of extractions	Vol. of butyric acid in ml	pH of the solution after addition of butyric acid	BeO in solvent in mg
1	25	3.80	27.4 ± 0.2
1	30	3.75	28.4 ± 0.2
2	25	3.80	28.8 ± 0.2
2	30	3.75	29.8 ± 0.2
3	30	3.75	29.0 ± 0.2

TABLE V

Amount of beryllium:	29.0 mg of BeO
Amount of iron:	19.4 mg of Fe_2O_3
Amount of aluminium:	29.7 mg of Al_2O_3
Complexon:	6 ml of 10% solution
Chloroform for each extraction:	50 ml

Vol. of sat. KCl	Vol. of butyric acid in ml	pH after addition of butyric acid	No. of extractions	BeO recovered
10	30	3.82	2	28.3 ± 0.3
20	30	3.81	2	28.3 ± 0.3
20	35	3.80	2	28.4 ± 0.3
10	40	3.73	3	29.0 ± 0.3

TABLE VI

ANALYSIS OF BERYL

	Results obtained in this laboratory by other methods	Results obtained in other laboratories	Results obtained by this method
Beryl I	12.95%	13.00%	13.04%:13.00%
Beryl II	12.88%	12.85%	12.84%:12.90%

ACKNOWLEDGEMENT

The authors wish to thank the Chairman, Atomic Energy Commission of India for permission to publish these results.

References p. 259.

SUMMARY

Quantitative extractions of aluminium and ferric ions are carried out in presence of butyric acid. A method has been given for quantitative extraction of beryllium from aluminium and ferric ion in presence of ethylenediaminetetra-acetic acid. Interference has been studied and interference due to phosphate has been avoided by addition of zirconium salt. The method has been applied to the analysis of beryl.

RÉSUMÉ

Une extraction quantitative des cations aluminium et fer(III) peut être effectuée en présence d'acide butyrique. Une méthode est proposée pour l'extraction du béryllium d'avec l'aluminium et le fer en présence d'acide éthylènediaminotétracétique. La spécificité des réactions est examinée; les phosphates gênent; ils sont éliminés par addition d'un sel de zirconium. La méthode a été appliquée à l'analyse du béryl.

ZUSAMMENFASSUNG

Es wurden quantitative Extraktionen von Aluminium und Ferriionen in Gegenwart von Buttersäure durchgeführt. Eine Methode zur quantitativen Extraktion des Berylliums von Eisenionen und Aluminium in Gegenwart von Äthylendiamintetraessigsäure wurde gegeben. Die Spezifität der Reaktion wurde untersucht und die störenden Phosphationen durch Zusatz von Zirkonsalz entfernt. Die Methode wurde zur Analyse des Berylls angewandt.

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DIRECT HETEROMETRIC MICRO-DETERMINATION OF ZINC WITH QUINALDIC ACID IN THE PRESENCE OF OTHER METALS

by

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INTRODUCTION

There are many studies dealing with the determination of zinc or copper with quinaldic acid, generally by gravimetric and to a smaller extent, by polarographic methods. The interference of other metals was studied[1].

The following investigation was made in order to study the heterometric[2] sensitivity and the suitability of quinaldic acid for the determination of zinc[1] by the heterometric method. The results given in Table I represent only a fraction of the titrations made. The study is of a general character and no attention was paid to special cases for which further experiments have to be made. Tartrate was mostly used as masking agent and therefore the determinations were made in neutral salt solutions. The reaction studied is not of the highest sensitivity in comparison with many other reactions which have been studied by us heterometrically. In this, as in many other cases, no parallel can be drawn between gravimetric and heterometric reactions. There are very many factors which are of importance during a gravimetric determination but are of no significance for a heterometric determination, and vice versa. With the exception of single cases, zinc can be determined directly in solutions which contain more than 90% of other bivalent or trivalent metals. The determination in the presence of nickel or cobalt is very limited. The heterometric titration of zinc with quinaldate, at room temperature, takes between 10 and 30 minutes, but this depends partly on the experience already gained in heterometry. By making a series of zinc determinations the titration time may probably be cut by half. In no case were filters used for the determination, even in the presence of strongly coloured solutions, as it was assumed that the supplementary metals do not interfere with the titration.

APPARATUS AND CHEMICALS

A "Heterometer", which was constructed by the first author, was used. The reaction vessel had a diameter of 3.6 cm and the absorption layer was approximately equal to one cm. A 5 ml microburet (0.01 ml) was used for the titration with

TABLE I

General composition: 3 ml 0.01M Zinc salt + 7 ml Supplements + X ml 0.02M Na-Quinaldate

Content: 1.96 mg Zn. Theoretical value: 3.16 ml Na-Quinaldate. Temp.: 23-25° C.

			%						
Exper. number	Salt used	Supplements	Zn	Suppl. metals	begin. of precip. at ml	Max. density value	Found ml	Approx. titration time min	% error
1	$ZnSO_4$	7 ml H_2O			0.0	0.55	3.16	20	
2	$ZnCl_2$	7 ,, ,,			0.0	0.51	3.15	25	—0.3
3	$ZnSO_4$	7 ,, ,, (content: 3 ml 0.005M)			0.0	0.5	1.62	10	2.4
4	,,	5 ,, ,, (content: 5 ml 0.01M). theoret. = 5.30 ml			0.0	1.05	5.44	20	2.5
5	,,	5 ,, ,, + 2 ml 1M Na_2-tartrate			0.4	0.41	3.18	25	+0.6
6	,,	2 ,, ,, + 5 ml alcohol			0.4	0.60	3.18	30	+0.6
7	,,	6 ,, ,, + 1 ,, 1M CH_3-COOH			0.5	0.34	3.2	20	+1.2
8	,,	4 ,, ,, + 3 ,, 1M $MgCl_2$	2.6	97.4	0.0	0.73	3.18	25	+0.6
9	,,	4 ,, ,, + 3 ,, 1M $CaCl_2$	1.6	98.4	0.0	0.65	3.14	15	—0.6
10	$ZnCl_2$	4 ,, ,, + 3 ,, 1M $BaCl_2$	0.5	99.5	0.4	0.55	3.16	15	0.0
11	$ZnSO_4$	4 ,, ,, + 3 ,, 1M $MnCl_2$	1.2	98.8	0.8	0.33	3.17	30	+0.3
12	,,	6 ,, ,, + 1 ,, 0.1M $NiCl_2$	25	75	3.2	∾0.8		25	
13	,,	6 ,, ,, + 1 ,, 0.1M $CoCl_2$	24.9	75.1	0.7	0.31	∾3.2	25	
14	,,	4 ,, ,, + 1 ,, 0.1M $CdSO_4$ + 2 ml 1M Na_2-tartrate	14.9	85.1	1.3	0.30	3.18	25	+0.6
15	,,	4 ,, ,, + 1 ml 1M $FeCl_3$ + 2 ml 1M Na_2-tartrate	3.4	96.6	0.5	0.44	3.18	40	+0.6
16	,,	4 ,, ,, + 1 ml 1M $AlCl_3$ + 2 ml 1M Na_2-tartrate	6.8	93.2	0.6	0.44	3.15	25	—0.3
17	,,	4 ,, ,, + 1 ml 1M $Cr(NO_3)_3$ + 2 ml 1M Na_2-tartrate	3.6	96.4	0.2	0.44	3.20	40	+1.2

quinaldate. The tip of the buret was immersed in the solution. The quinaldic acid BDH "for spot tests" was dissolved in water and then neutralised to pH ∿ 7.0 with NaOH. Other chemicals used were all either analytically or chemically pure. The reaction temperature was 23-25° C.

RESULTS

In Table I are compiled the results of a selection of the titrations. The course of the titrations for some experiments are given in Fig. 1 (the experiment numbers are the same in Table I and Fig. 1). In order to give a more detailed account of the results we prefer to discuss each case separately.

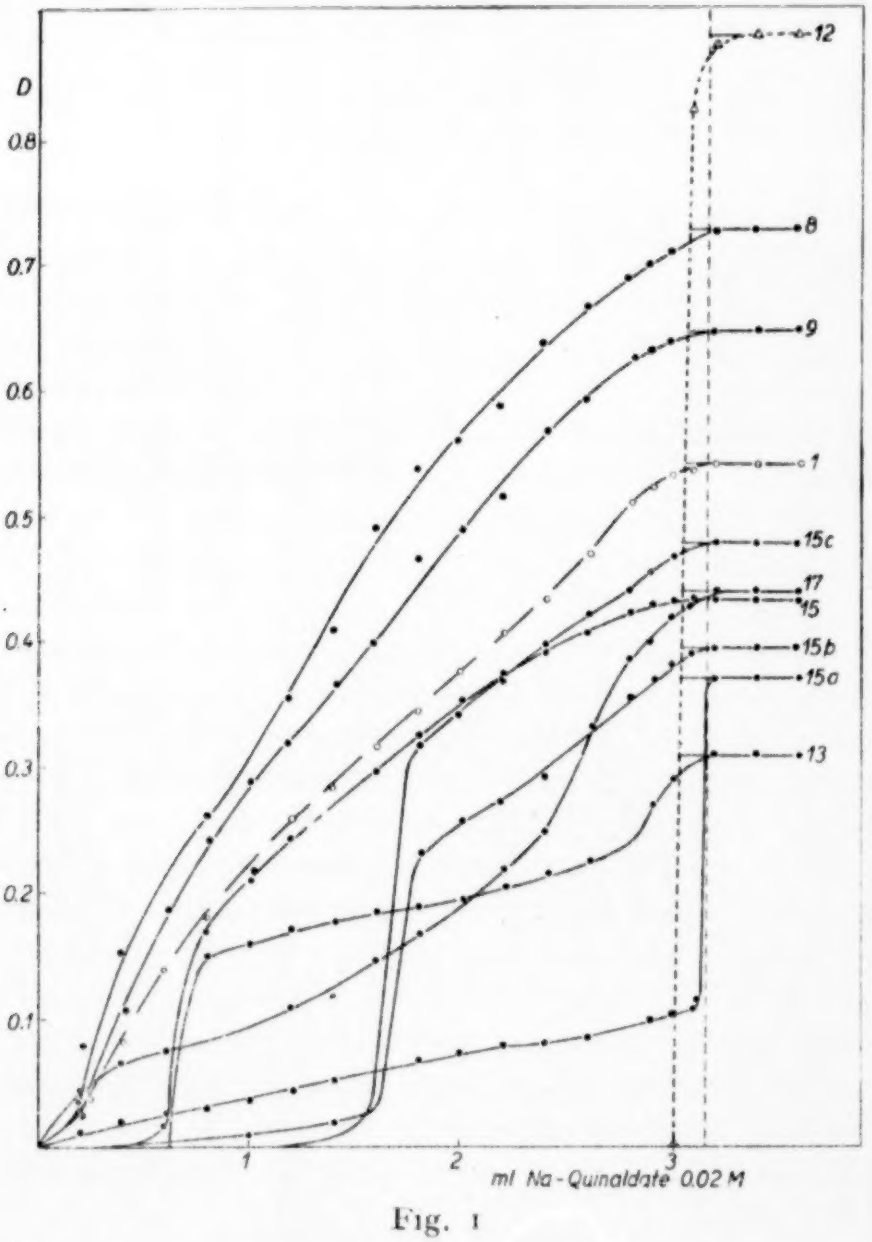

Fig. 1

Zinc determination in the absence of other metals

Under our working conditions (10 ml analysed volume; light absorption layer ∿ 1 cm) 1-4 mg (Zn^{+2}-concentration: 0.001*M*-0.005*M*) can be determined in

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a neutral Zn-solution generally with an error of $\leq$ 1%. The presence of 0.2*M* Na_2-tartrate (exp. 5) is of no influence. The maximum optical density value seems to decrease in the presence of 0.1*M* acetic acid (exp. 7). 50% alcoholic solution has no clear influence although the titration time is somewhat longer. In the presence of Na_3-citrate the titration takes longer and the results are also not certain.

In the presence of Ca^{+2}, Ba^{+2} *or* Mg^{+2}

These metals may be present in large excesses (97-99%) (exps. 8-10). The heterometric titration of zinc proceeds more rapidly than in the absence of these salts and the maximum density values obtained are even higher than the blank.

In the presence of Mn^{+2}

Approximate theoretical results are obtained although the maximum density value seems to be low (exp. 11).

In the presence of Ni^{+2} *or* Co^{+2}

If the concentration is 0.05-0.1*M*, no precipitation occurs. In 0.01*M* Co-solution the endpoint of zinc determination can be obtained but the density seems to be low, (exp. 13). No precipitation of zinc occurs during the titration if 0.01*M* nickel is present (exp. 12). Exactly at the calculated endpoint of the titration (= 1 Zn : 2 Quinaldate) a precipitate occurs and the optical density rises abruptly and considerably. This point can, therefore, be used for the determination of zinc which can be made without a heterometer. Titrations were made in the presence of excess Na_2-tartrate but no precipitation of zinc occurred.

In the presence of Cd^{+2}

Zinc may be determined in excesses of Cd (= 85%) if the solution contains an excess of Na_2-tartrate (exp. 14).

In the presence of Al^{+3}, Fe^{+3} *or* Cr^{+3}

An excess of Na_2-tartrate was added to all solutions (exps. 15-17). The solution which contained 93.2% aluminium could be titrated with precision (exp. 16). Although on the addition of excess Na_2-tartrate to iron solutions (96.6%) a deep red solution was obtained (exp. 15), the endpoint of the zinc titration could be defined with precision. An additional titration for comparison with 1 ml 0.5*M* $FeCl_3$ was made (curve 15b). Here too, a clear endpoint was obtained. Both experiments were repeated using a deep red filter. In both cases the endpoint could be obtained with precision. As curve 15a (1 ml 1*M* $FeCl_3$ with red filter) shows, an abrupt increase in the optical density occurs exactly at the endpoint of the titration. The use of a filter is therefore of no practical value.

In the presence of chromium (96.4%) (exp. 17) a curve of complex character is obtained, but in spite of this, the endpoint can be determined (error 1.2%). The character of these curves requires further study.

On the accuracy of the zinc determination

The volume in ml of quinaldate which is required in order to obtain the first maximum optical density point were taken from enlarged curves. In each case a line was drawn through the points obtained in the last part of the titration. The point of intersection of this line with the horizontal maximum density line, was taken as the endpoint of the titration. In almost all cases the error was within 1%. By repeating titrations with the same metal, the accuracy of the determination may be increased. As experiments 3 and 4 show, the error increases considerably if too small quantities of quinaldate are used (exp. 3) or if the maximum density value is too high (exp. 4). In the latter case an absorption vessel of a larger diameter should be used.

In almost all cases the point of initial precipitation is near the beginning of the titration. If this point is near the end of the titration, the determination may become uncertain. This is the case with nickel. Cd also causes a partial dissolution of zinc quinaldate and the point of the initial precipitation is shifted to the end. Probably in the presence of somewhat more cadmium, the precipitation of zinc may be avoided.

SUMMARY

0.001-0.005*M* solutions of zinc salts (1-5 mg Zn in 10 ml) which contain more than 95% of foreign metal as Mg, Ca, Ba, Mn(II), Fe(III), Al or Cr(III), may be titrated heterometrically with an error of $\leqslant$ 1%. The titrated zinc solution may contain an excess of Cd (85%). The analysis with Ni or Co is very limited.

RÉSUMÉ

On peut titrer hétérométriquement, avec une précision de $\leqslant$ 1% des solutions 0.001-0.005*M* de sels de zinc (1-5 mg zinc dans 10 ml) et contenant plus que 95% de métaux étrangers, tels que Mg, Ca, Ba, Mn(II), Fe(III), Al ou Cr(III). La solution de zinc à titrer peut contenir un excès de Cd (85%). L'analyse est très limitée en présence de Ni et Co.

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0.001-0.005*M* Zinksalzlösungen (1-5 mg Zn in 10 ml), welche mehr als 95% Fremdmetalle wie Mg, Ca, Ba, Mn(II), Fe(III), Al oder Cr(III) enthalten, können heterometrisch mit einem Fehler von $\leqslant$ 1% titriert werden. Die zu titrierende Zinksalzlösung kann überschüssiges Cd (85%) enthalten. Die Analyse in Gegenwart von Ni oder Co ist beschränkt.

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PRÉVISION DES COURBES DE DOSAGE PAR POTENTIOMÉTRIE BIMÉTALLIQUE AU MOYEN DES COURBES DE POLARISATION

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Dans un mémoire précédent[1] nous avons montré comment les courbes de polarisation permettaient d'étudier et d'interpréter les courbes des dosages potentiométriques classiques, c'est-à-dire lorsque l'on mesure la différence de potentiel existant entre une électrode indicatrice immergée dans une solution oxydo-réductrice et une électrode de référence. Dans le présent mémoire, nous nous proposons d'envisager le cas des dosages par électrodes bimétalliques, c'est-à-dire lorsque l'on suit la différence de potentiel existant entre deux électrodes indicatrices de natures différentes immergées dans la solution oxydo-réductrice.

En effet, on a observé que les indications de deux électrodes de métaux non-identiques diffèrent au voisinage du point équivalent, cette différence passant par un maximum en ce point. HOSTETTER ET ROBERTS[2] ont les premiers suggéré l'utilisation d'électrodes bimétalliques pour détecter la fin des dosages. Depuis, de nombreux couples d'électrodes ont été décrits ainsi que de nombreux modes opératoires.

FORME DES COURBES DE DOSAGE

Nous appelons corps électroactif vis-à-vis d'une électrode un corps dont on peut tracer la courbe de polarisation sur l'électrode envisagée.

Lorsque les formes réduite et oxydée d'un même système sont électroactives, une électrode inattaquable plongée dans une solution contenant les deux formes indique un potentiel d'équilibre, indépendant de la nature de l'électrode comme l'a montré en particulier PIONTELLI[3]. Par contre, si une des formes n'est pas électroactive, l'électrode indique un potentiel mixte qui est fonction de sa nature physico-chimique[4].

Nous envisagerons quatre cas possibles lorsqu'on utilise deux électrodes inattaquables.

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a. *Les formes réduites et oxydées des deux systèmes sont électroactives vis-à-vis des deux électrodes*

De part et d'autre du point équivalent les deux électrodes sont au même potentiel puisqu'elles indiquent le potentiel d'équilibre du système titrant ou titré. Au point équivalent les concentrations des corps titrant et titré sont inférieures à leur concentration limite et les deux électrodes indiquent un potentiel mixte qui est fonction de leur nature.

Donc, la différence de potentiel entre les deux électrodes doit être nulle de part et d'autre du point équivalent et avoir une valeur différente de zéro, mal définie d'ailleurs, au voisinage de ce point (courbe *a* Fig. 1).

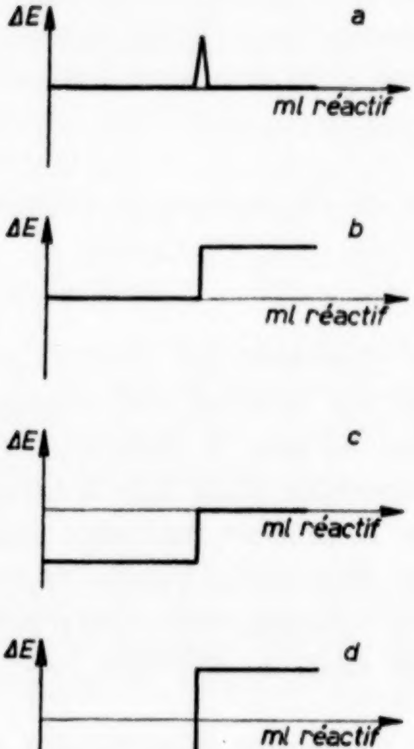

Fig. 1. Courbes théoriques.

b. *Le système titrant n'a qu'une forme électroactive*

Dans ce cas, la différence de potentiel entre les deux électrodes peut persister du fait même qu'après le point équivalent, celles-ci indiquent un potentiel mixte (courbe *b* Fig. 1).

c. *Le système titré n'a qu'une forme électroactive*

Cette fois, c'est avant le point équivalent que la différence de potentiel entre les deux électrodes est différente de zéro (courbe *c* Fig. 1).

d. *Les systèmes titrant et titré n'ont qu'une forme électroactive*

La différence de potentiel n'est jamais nulle. Elle passe par un maximum ou un minimum au point équivalent où il n'existe plus en solution aucun corps électroactif (courbe *d* Fig. 1).

Remarquons que la Fig. 1 ne représente que des courbes théoriques. En effet, celles-ci peuvent présenter un maximum ou un minimum au point équivalent. De plus, dans le cas *d*, par exemple, la différence de potentiel peut garder le même signe de part et d'autre du point équivalent.

EXEMPLES DE COURBES EXPÉRIMENTALES

Nous avons envisagé le couple d'électrodes platine-graphite.

Les mesures sont effectuées de la façon suivante: après chaque addition de réactif, le potentiel des électrodes est déterminé par rapport à une électrode au calomel à l'aide d'un potentio-pHmètre M.E.C.I. Ensuite, les deux électrodes indicatrices sont reliées aux bornes de l'appareil et la différence de potentiel entre celles-ci est directement mesurée. En aucun cas l'écart observé entre la différence des potentiels mesurée directement et celle obtenue à partir des valeurs déterminées par rapport à l'électrode au calomel ne dépasse 2 mV. Les potentiels pouvant varier au cours du temps, en particulier au voisinage du point équivalent, ceux-ci sont déterminés deux minutes après la nouvelle addition de réactif.

Lorsque le potentiel de l'électrode de graphite est supérieur à celui de l'électrode de platine, leur différence est comptée positivement et négativement dans le cas contraire.

Les quatre formes sont électroactives

Nous avons envisagé le cas des systèmes Fe(II)/Fe(III) et V(IV)/V(V) où les quatre ions correspondants sont électroactifs vis-à-vis des deux électrodes utilisées[4].

La courbe de dosage de 10 ml d'une solution de sel de Mohr 0.1086N en milieu sulfurique M par une solution de vanadate 0.1063N est représentée Fig. 2. On constate que de part et d'autre du point équivalent, la différence de potentiel entre les deux électrodes est nulle (à 1 mV près).

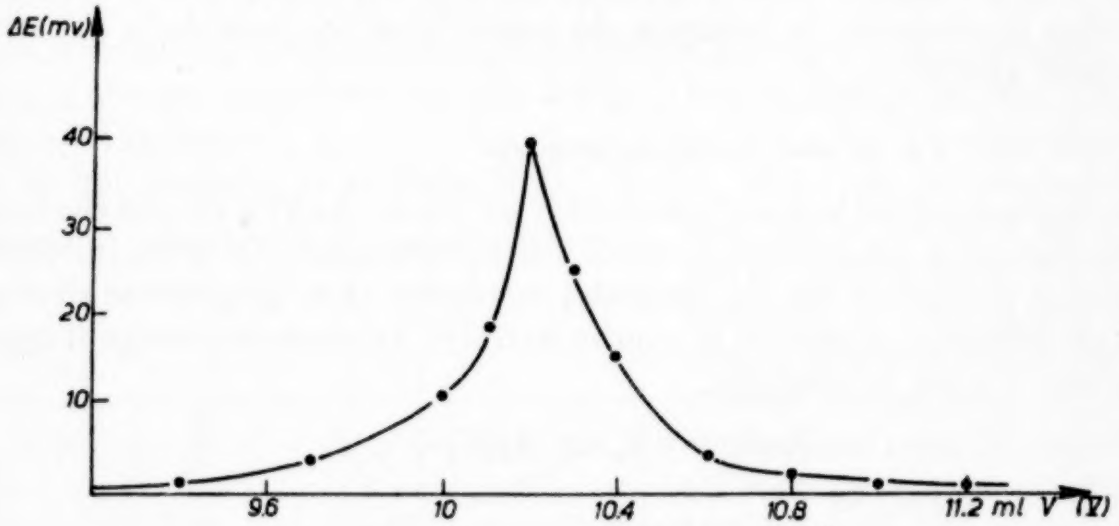

Fig. 2. Courbe de dosage de Fe(II) par V(V).

Le maximum de △E correspond à 0.2% près au point équivalent déterminé sur les courbes représentant la variation du potentiel en fonction de la quantité de vanadate ajouté.

Le système titrant n'a qu'une forme électroactive

C'est le cas du dosage du fer ferreux par le bichromate.

Les ions de Cr(III) ne sont pas électroactifs. Sur la Fig. 3. sont représentées

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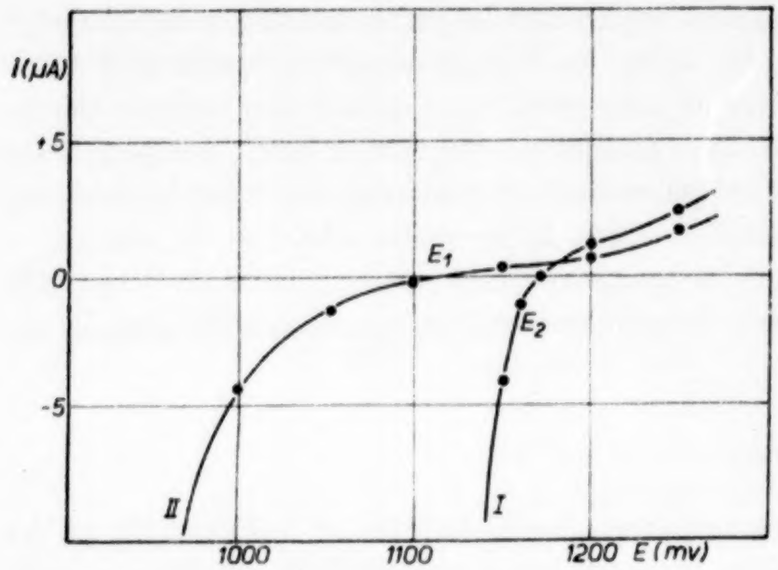

Fig. 3. I: Réduction de $Cr_2O_7^{-2}$ sur graphite.
II: Réduction de $Cr_2O_7^{-2}$ sur platine.

les courbes de polarisation du bichromate 0.1N en milieu sulfurique M sur des électrodes de platine et de graphite.

Au cours du dosage envisagé, la différence de potentiel entre les deux électrodes doit persister après le point équivalent, l'électrode de graphite ayant le potentiel le plus élevé ($E_2 > E_1$, Fig. 3), ce que l'on peut observer sur la courbe (Fig. 4) obtenue lors du dosage de 10 ml de sel de Mohr 0.0840N en milieu sulfurique M par une solution de bichromate 0.1008N.

Le saut de potentiel observé Fig. 4 correspond à 0.3% près à celui obtenu avec les courbes représentant la variation du potentiel en fonction de la quantité de bichromate ajouté.

Le système titré n'a qu'une forme électroactive

Nous avons envisagé le dosage de As(III) par l'iode. As(V) n'est pas électroactif.

Cependant dans cet exemple il existe une complication. En effet, la courbe de polarisation de l'iodure sur les électrodes de platine et de graphite se situe à des potentiels inférieurs à ceux de la courbe As(III)[1]. Au cours du dosage il apparaît de l'iodure d'après la réaction;

$$As(III) + I_2 \rightleftarrows As(V) + 2\ I^-$$

de sorte qu'avant le point équivalent on mesure un potentiel mixte non pas entre As(III) et l'oxygène, mais entre I^- et As(III) d'une part et l'oxygène d'autre part. De toute façon la courbe de dosage sera du type *c* Fig. 1.

La courbe obtenue lors du dosage de 10 ml d'une solution d'acide

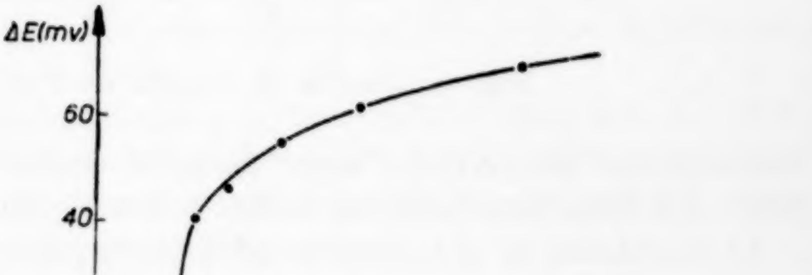

Fig. 4. Courbe de dosage de Fe(II) par Cr(VI).

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arsénieux $0.0916N$ par une solution d'iode $0.0985N$ à pH 8 (bicarbonate de sodium) est représentée Fig. 5.

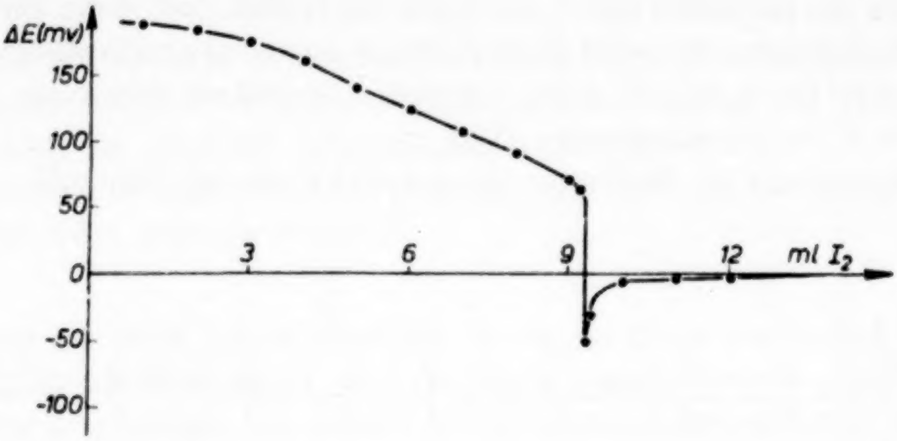

Fig. 5. Courbe de dosage de As(III) par l'iode.

Les deux systèmes n'ont qu'une forme électroactive

Nous n'avons pas trouvé d'exemple correspondant à ce cas. Cependant il est possible d'obtenir une courbe du type *d* Fig. 1 lors du dosage de l'eau oxygénée par le permanganate.

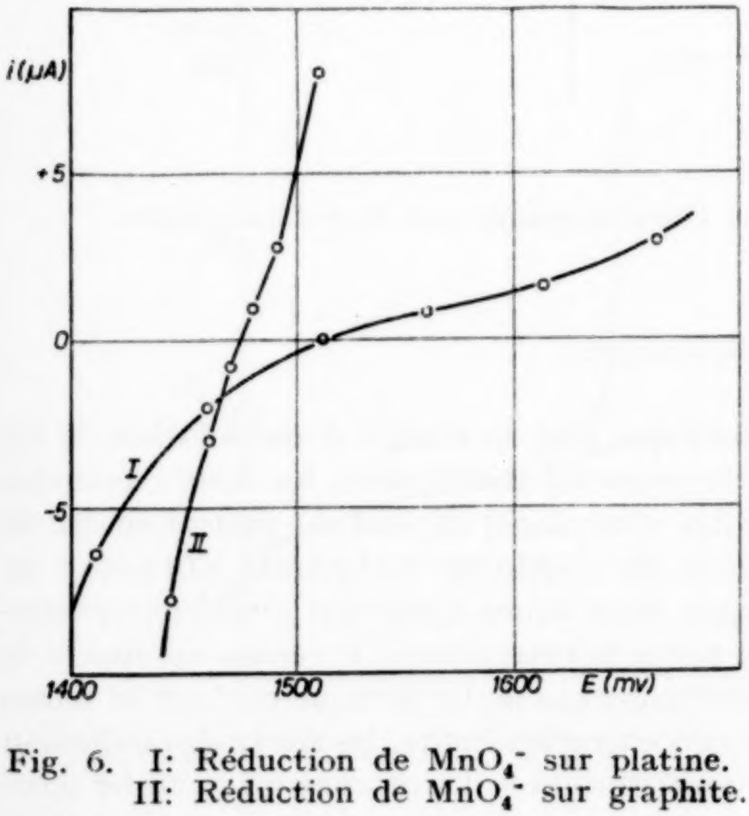

Fig. 6. I: Réduction de MnO_4^- sur platine.
II: Réduction de MnO_4^- sur graphite.

En ce qui concerne le système $MnO_4^-/Mn(II)$, seul l'ion permanganique est électroactif vis-à-vis des électrodes de platine et de graphite, le potentiel à courant nul obtenu avec la première étant supérieur à celui obtenu avec la seconde comme on peut le voir Fig. 6, où sont tracées les courbes correspondantes en milieu sulfurique M.

Pour le système H_2O_2/O_2, il est possible de tracer les courbes de polarisation des deux formes sur une électrode de platine. Cette dernière lorsqu'elle est plongée dans une solution d'eau oxygénée à l'air doit donc indiquer, en principe, un potentiel d'équilibre. Par contre, au même pH, l'eau oxygénée ne semble pas être électroactive vis-à-vis de l'électrode de graphite, ou tout au moins sa courbe d'oxydation est voisine de celle de l'eau. Donc une électrode de graphite indique un potentiel mixte dans une solution aérée d'eau oxygénée.

La différence de potentiel entre les deux électrodes doit donc être différente de zéro de part et d'autre du point équivalent, ce que nous avons observé en titrant 30 ml d'une solution 0.0373*N* d'eau oxygénée en milieu sulfurique *M* par une solution 0.1300*N* de permanganate (Fig. 7).

Au point équivalent la différence de potentiel atteint 650 mV.

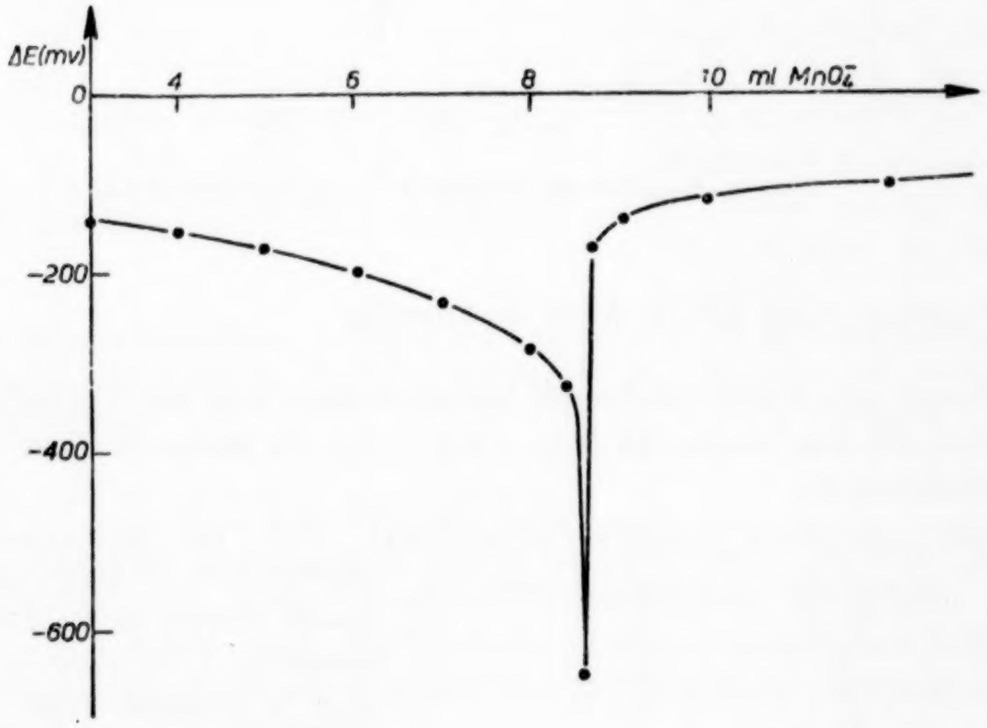

Fig. 7. Courbe de dosage de l'eau oxygénée par le permanganate.

REMARQUES

Willard et Fenwick[5] observèrent que lors du dosage d'une solution de fer ferreux par le bichromate l'écart de potentiel initial entre les deux électrodes (avant addition de la première goutte d'oxydant) dépend du prétraitement de celles-ci et tombe rapidement à zéro dès l'addition d'oxydant. Kolthoff et Laitinen[6] ont fait la même remarque. Nous avons également observé ce phénomène lors du dosage du fer ferreux par le permanganate, le cérium cérique et le vanadate. La solution initiale ne contenant pas de fer ferrique ou tout au moins à une concentration inférieure à sa concentration limite, les électrodes indiquent le potentiel limite du fer ferreux (potentiel mixte). La concentration du fer ferri-

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que est pratiquement supérieure à sa concentration limite (10^{-5} ion-g/litre) dès l'addition d'une ou deux gouttes d'oxydant et les électrodes indiquent un potentiel d'équilibre.

Lorsque les quatre corps mis en jeu sont électroactifs l'écart entre les indications des deux électrodes n'est différent de zéro qu'au voisinage du point équivalent. On risque donc de dépasser celui-ci sans s'en apercevoir.

Dans tous les dosages pratiques indiqués par MÜLLER ET KOGERT[7] au moins un des corps n'est pas électroactif.

Nous avons envisagé jusqu'à présent le cas de deux électrodes inattaquables. Or il est fréquent d'employer une électrode passivable; le potentiel de cette dernière varie peu lorsque la solution est devenue suffisamment oxydante, tandis que l'électrode inattaquable continue de fonctionner comme électrode indicatrice. On observe donc toujours un saut de potentiel au point équivalent.

A titre indicatif nous représentons les courbes de dosage du fer ferreux par le vanadate avec des électrodes de platine et de molybdène (Fig. 8) et la courbe représentant la différence de potentiel entre celles-ci en fonction de la quantité de vanadate ajouté (Fig. 9).

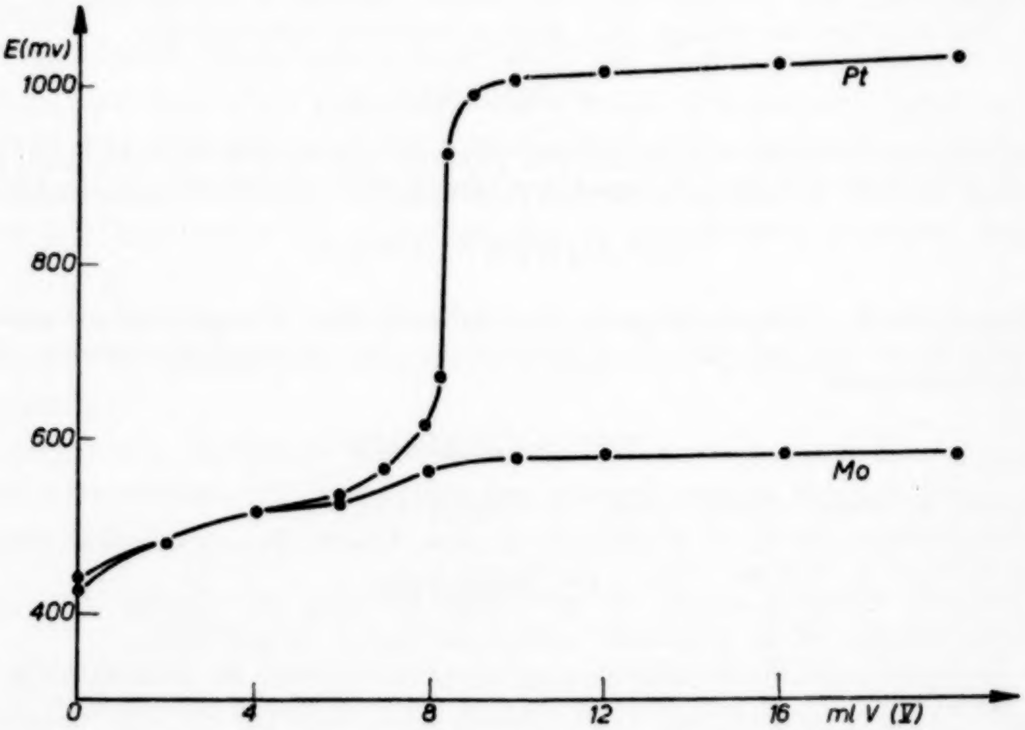

Fig. 8. Courbes de dosage de Fe(II) par V(V) avec des électrodes de platine et de molybdène.

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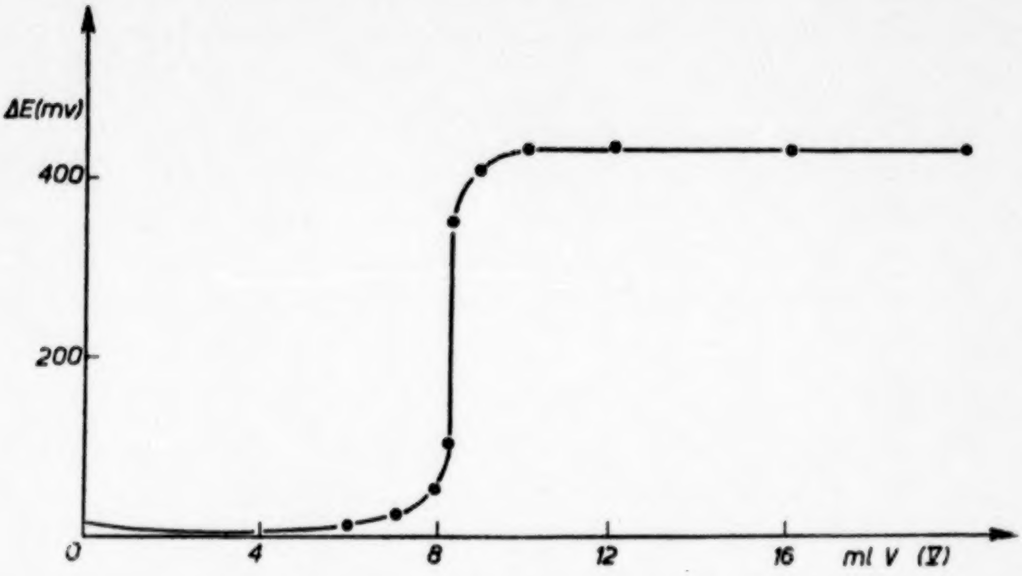

Fig. 9. Dosage de Fe(II) par V(V). Couple d'électrodes Pt-Mo.

Quel que soit le fonctionnement des électrodes, et que les corps entrant en réaction soient électroactifs ou non vis-à-vis d'une seule ou des deux électrodes, les courbes de dosage se ramènent toujours à l'une des quatre courbes théoriques représentées Fig. 1.

RÉSUMÉ

La connaissance des courbes de polarisation permet d'interpréter et de prévoir la forme des courbes de dosage par potentiométrie bimétallique.

SUMMARY

The knowledge of polarisation curves permits the interpretation and prediction of the form of the curves obtained by bimetallic potentiometric determination.

ZUSAMMENFASSUNG

Die Kenntnis der Polarisationskurven erlaubt die Interpretation und die Voraussage der Form der bei der Potentiometrie mit Bimetallelektroden erhaltenen Bestimmungskurven.

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THE POLAROGRAPHIC DETERMINATION OF MANGANESE, COPPER, CHROMIUM AND IRON IN THE INSOLUBLE RESIDUE REMAINING AFTER THE SOLUTION OF CALCIUM METAL IN HYDROCHLORIC ACID

by

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INTRODUCTION

In a previous paper describing the determination of copper, lead, chromium, cadmium and manganese in calcium metal[1] it was noted that an insoluble residue often remains when the calcium metal is dissolved in hydrochloric acid. For the purposes of the determination it was satisfactory to allow the solution to stand overnight and then to filter off the residue and dissolve it separately by heating under reflux with fuming perchloric acid. The resulting solution was then added to the main bulk of the calcium solution for the determination of total impurities in the sample.

It had been shown spectrographically that the major constituent of the insoluble residue was chromium together with a small amount of copper and manganese, but it was desirable that some knowledge of the amounts of these metals should be available. From the literature it appeared possible that they could be determined simultaneously by polarography in an alkaline mannitol base electrolyte.

This investigation was therefore undertaken with the object of developing a method for the determination of copper manganese chromium and iron in the insoluble residue.

In this paper the European sign convention has been used throughout and, unless otherwise stated, all potentials are quoted versus the saturated calomel electrode (vs. S.C.E.)

EXPERIMENTAL

The determinations of the impurities in calcium metal are carried out on 50 g portions of the metal which are dissolved in hydrochloric acid[1]. Therefore 50 microgram of any element present in the insoluble matter is equivalent to a 1 p.p.m. content in the sample. It was originally hoped that the total residue would be concentrated in a final volume of solution of 10 ml, giving a concentration of 5 microg/ml for an amount of impurity equivalent to 1 p.p.m. in the calcium metal. The experimental work was, therefore, confined to concentrations up to 100 microg/ml for each element determined. For reasons that will be given later it was subsequently found necessary to increase the final volume of solution to 25 ml with consequent loss of sensitivity.

Standard solutions of copper, chromium iron and manganese were added to 2 ml fuming perchloric acid in a boiling tube fitted with a "cold finger" condenser, of the type described in a previous paper[1]. The solution was heated for about 30 minutes and allowed to cool. 2 ml freshly prepared 15 per cent. mannitol and 3 ml 10 per cent. sodium hydroxide were then carefully added. The solution was made up to 10 ml in a graduated flask and polarographed, after deoxygenation, using the special research polarograph constructed in these laboratories[2]. The dropping mercury electrode employed had a drop time of 5 seconds and an $m^{2/3}\,t^{1/6}$ value of 1.69. It was already known that a drop time of this order was more satisfactory for alkaline solutions than the more conventional 2—3 seconds[3]. A 1.0M sodium chloride/calomel half-cell, or a 1.0M sulphuric acid/mercurous sulphate half cell were used as anode since a saturated calomel electrode causes precipitation of potassium perchlorate to occur at the liquid junction with the polarographic cell solution. The potentials of these two cells versus the saturated calomel electrode were measured by means of a potentiometer.

Satisfactory results were obtained for copper, iron and manganese, their half-wave potentials being close to the reported values. No wave due to chromium was, however, observed. It is known[3] that trivalent chromium does not give a reduction wave in alkaline mannitol solution and it was therefore assumed that the chromium added as chromate to the perchloric acid solution was being reduced before polarography. It was also shown experimentally that an acid dichromate solution will oxidise mannitol, being itself reduced to the chromic state. The perchloric acid was therefore neutralised before adding the mannitol but the added elements precipitated as hydroxide and did not re-dissolve. Many different methods of carrying out the additions of alkali and mannitol to the acid solution were therefore tried, all without success.

In view of this failure, the procedure already successfully used for the determination of iron and chromium in an alkaline mannitol medium[3] was adopted. This involved a considerable dilution of the perchloric acid solution (the final volume after the addition of alkali and mannitol being 25 ml) with consequent loss of sensitivity of the method. The attainable limits given in Table I were, however, sufficiently low for the method to be of use.

The limit of satisfactory determination was taken as that amount of the element which gave a step height of about 10 mm on the maximum sensitivity of the polarograph.

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TABLE I

Element	Limit of detection	Corresponding conc. in sample
Copper	1.0 microg/ml	0.5 p.p.m.
Chromium	0.25 microg/ml	0.125 p.p.m.
Iron	2.0 microg/ml	1.0 p.p.m.
Manganese	2.0 microg/ml	1.0 p.p.m.

Several mock insoluble residues were prepared, some from soluble salts of the metals and others from the most insoluble pure forms available. Three sets of analyses are given in Table II and a typical polarogram is shown in Fig. 1. In these results the blank due to reagents has been subtracted.

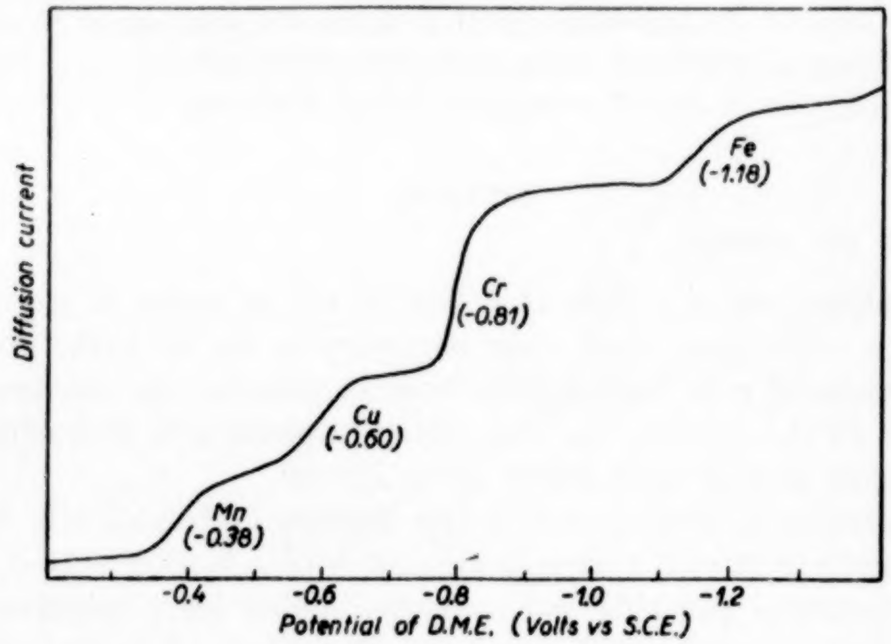

Fig. 1.
Polarogram of manganese, copper, chromium and iron in alkaline mannitol solution.

TABLE II

Element	Copper		Chromium		Iron		Manganese	
Sample	p.p.m. added	p.p.m. found	p.p.m. added	p.p.m. found	p.p.m. added	p.p.m. found	p.p.m. added	p.p.m. found
1	6.1	5.9	6.8	5.4	1.9	1.95	2.1	2.0
2	12.8	11.9	4.0	3.8	8.4	7.8	4.9	4.2
3	4.8	5.0	13.0	12.7	15.7	14.9	12.2	11.4

Several 50 g portions of different samples of calcium metal were then dissolved in hydrochloric acid. Some were filtered immediately and then again after being allowed to stand overnight, while others were filtered only after prolonged standing. Some typical results of these analyses are given in Table III. For these determinations the final procedure, given below, was used.

TABLE III

Sample	Treatment	Copper	Chromium	Iron	Manganese
1	a.	0.5 p.p.m.	3.2 p.p.m.	—	1.0 p.p.m.
1	b.	—	0.2 p.p.m.	—	—
2	c.	—	—	1.0 p.p.m.	—
3	d.	0.5 p.p.m.	5.4 p.p.m.	—	1.8 p.p.m.

Where no figures are quoted the element was not detected.

Notes on treatment

a. Solution filtered immediately after preparation.
b. Filtrate from a. refiltered after standing overnight.
c. Solution allowed to stand overnight before filtering.

METHOD

Preparation of the sample

Add 50 g calcium metal a little at a time to 100 ml water in a 900 ml beaker covered with a clock glass. Cool when necessary in an ice bath. From time to time add portions of 10*M* hydrochloric acid to dissolve the calcium hydroxide formed. When all the calcium has been added carefully add hydrochloric acid to make the volume of 10*M* acid added up to 250 ml.

Heat the solution to boiling, and if any calcium hydroxide still remains add further 5 ml portions of 10*M* hydrochloric acid until it is all dissolved. Add 0.5 ml 100 volume hydrogen peroxide and continue boiling for 5 minutes. Allow the solution to stand overnight and filter through a Buchner funnel using a 9 cm No. 42 Whatman filter paper.

Dry the filter paper and residue and transfer it to a silica crucible. Ignite over a bunsen flame to bright red heat until no carbon remains. Transfer the contents to a boiling tube fitted with a "cold finger" condenser, add 2.0 ml 12*M* perchloric acid to the tube and heat gently until all the residue is dissolved (Note 1).

Transfer the contents of the tube to a 25 ml graduated flask. Rinse down the "cold finger" condenser and tube with 6 ml 2*M* sodium hydroxide and add the rinsings to the flask. Add a mixture of 5 ml 15 per cent. mannitol solution and 5 ml 10*M* sodium hydroxide solution. Make up to volume with water.

Transfer a portion of the solution to a polarographic cell deoxygenate and record a polarogram over the range —0.4 to —1.7 volts (note 2) at 25° C using a 1.0*M* sulphuric acid/mercurous sulphate half-cell as anode and a drop time for the mercury cathode of about 6 seconds. Measure the heights of the steps due to manganese, copper, chromium and iron, which occur with half-wave potentials of —0.78, —1.0, —1.2, and —1.5 volts respectively (note 3), obtain the concentrations of each element in the original sample by means of calibration factors obtained by determinations carried out on suitable standard solutions.

Notes

1. If silica is present in the sample it will not be dissolved and must be ignored.
2. It is desirable, in view of the closeness of the steps and the high instrumental sensitivity setting necessary for the determination, that an extended voltage scale such as described by BRYANT AND REYNOLDS be used[2]. This is especially useful in the case of manganese and copper.
3. Slight mutual interference exists between some of the steps obtained (especially manganese and copper). Results are improved if an intersection method of measurement is employed. This is illustrated in Fig. 2.

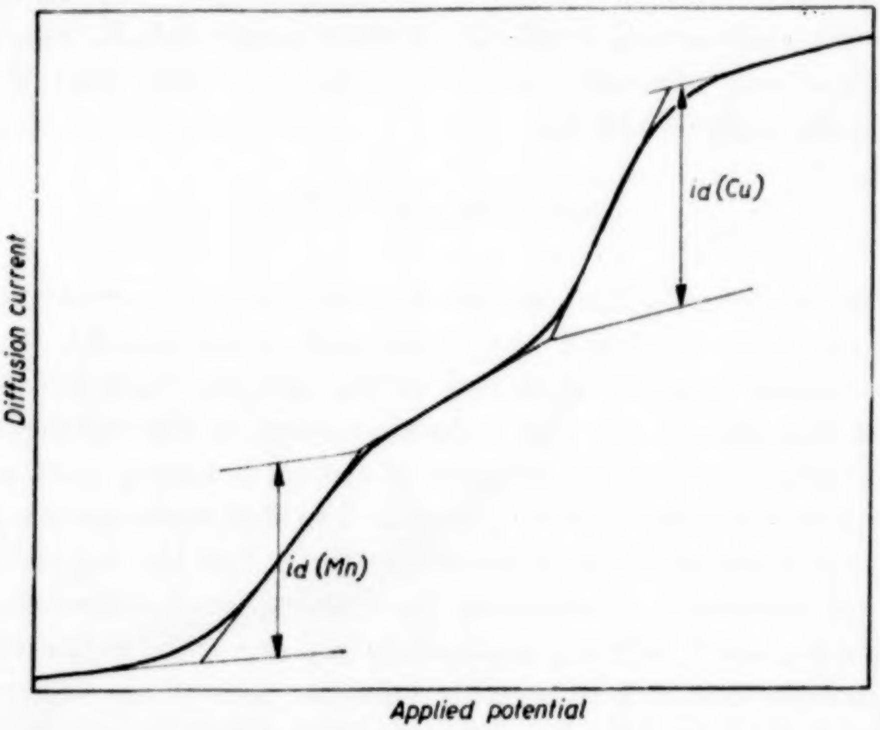

Fig. 2. Intersection method of step-height measurement (applied to the manganese and copper steps).

DISCUSSION

The polarography of iron and copper in alkaline mannitol was investigated by WINTERTON AND MAKER in an Admiralty Laboratory. They found half-wave potentials of —1.2 volts and —0.6 volts for iron and copper respectively. They also found half-wave potentials of —0.85 volts for hexavalent chromium and and —0.4 volts for manganese. The medium they employed was approximately $2M$ with respect to potassium hydroxide and 6 per cent. with respect to mannitol.

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PERKINS AND REYNOLDS[3] have investigated the polarography of iron and chromium in a medium approximately $3M$ with respect to potassium hydroxide and 3 per cent. with respect to mannitol. Half-wave potentials of —1.12 volts and —1.74 volts ($Fe(II) \rightarrow Fe$) for iron and —0.83 volts for chromium were reported. All these values compare favourably with those obtained in the present work, which were: manganese —0.38 volts; copper —0.60 volts; chromium —0.81 volts and iron —1.18 volts. PERKINS AND REYNOLDS also investigated the effect of alkali concentration and the drop time of the mercury cathode on the general shape of the iron and chromium reduction steps. The optimum conditions were found to be an alkali concentration of $3M$ and a drop time of about 6 seconds. These values have, therefore, been specified in the method.

No information on the mechanism of the copper and manganese reductions in alkaline mannitol was available. In the case of copper it is known[4] that in complexing media such as ammonia chloride, thiocyanate etc. two reduction steps are obtained which are separated by about 0.25 volts and that the first of these steps generally occurs at about 0.0 volts versus S.C.E. Since we observe only one reduction step between 0.0 and 1.5 volts it is likely that the reduction occurring may be represented by:

$$\text{Cu(I) Complex} \rightarrow \text{Cu}$$

but since no thermodynamic data on the mannitol-copper complex are available, calculation of the theoretical half-wave potentials is not possible. Comparison of the diffusion current constant obtained in the alkaline mannitol solution with that obtained fom one of the two reduction steps of the cuprammonium ion, $[Cu(NH_3)_4]^{+2}$, indicates that the number of electrons taking part in the copper reduction is one, as the values are very similar. Further confirmation of this fact is obtained by a calculation of the diffusion coefficient of the copper-complex ion, assuming that 1 electron is involved in the reduction the diffusion coefficient is calculated to be $0.56 \cdot 10^{-5}$, which is approximately one-third of the value usual for monovalent cations. This is a reasonable value in view of the complexing which is occurring, and if n were greater than one, the diffusion coefficient would be absurdly small.

Similar calculations show that if more than one electron were involved in the magnanese reduction, then the diffusion coefficient of the manganese-mannitol complex ion would similarly be absurdly small, but even if a value of one is assumed, the diffusion coefficient is calculated to be $0.11 \cdot 10^{-5}$, which is only approximately one-fifth of the usual value for trivalent cations. Again no thermodynamic data are available to enable a calculation to be made of the possible theoretical half-wave potentials of the manganese reduction. However, manganese has been reported[5] to give a well defined anodic wave at —0.4 volts versus S.C.E. in a solution $2N$ with respect to sodium hydroxide and 5 per cent. with respect to sodium potassium tartrate. In this medium the manganese is *oxidised* at the dropping mercury *cathode* to the trivalent state and it is probable that the same reaction is occurring in the alkaline mannitol base solution. Additional experimental support for this mechanism is provided by the appearance of the manganese step. This has a large drop wave at the base of the step which decreases to a minimum just before the top. The zero diffusion current line has been shown to pass through this point of minimum drop wave (see Fig. 3). The electrode reaction may, therefore, be represented by:

$$\text{Mn(III) complex} \rightarrow \text{Mn(II) complex}$$

the step obtained being due to the fact that the oxidation ceases to occur. This oxidation proceeds at zero applied voltage and continues until the potential of the cathode reaches the negative value at which the step occurs, but this does not affect the height of the step as the oxidised complex is then reduced.

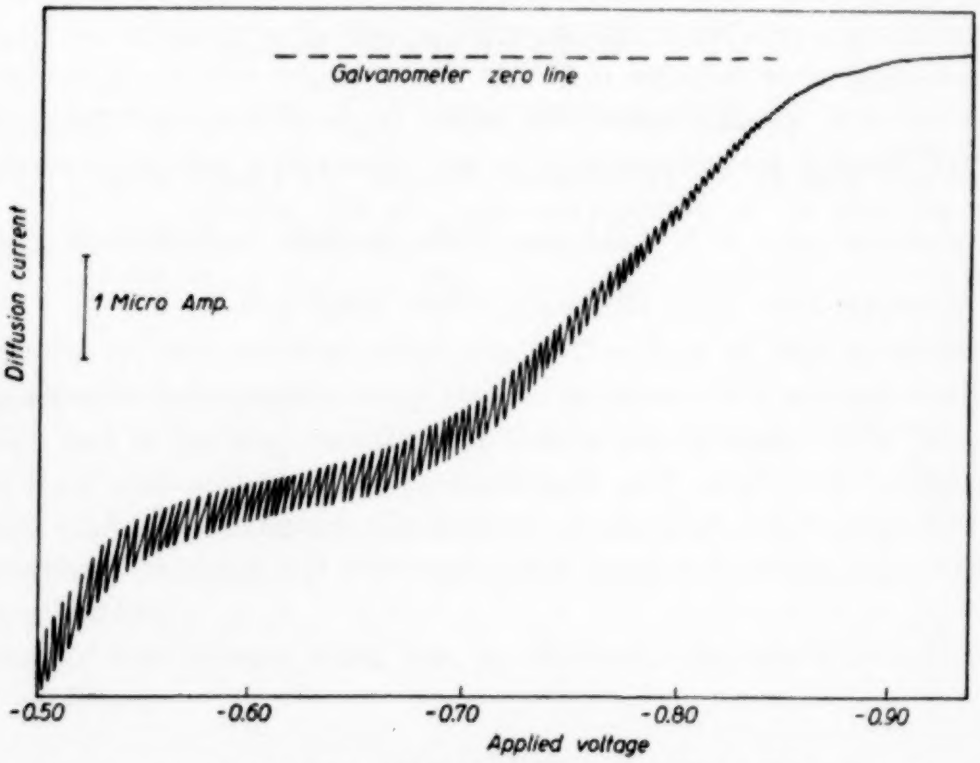

Fig. 3. Manganese (200 μg/ml) in $2M$ sodium hydroxide and 3 per cent. mannitol (versus M H_2SO_4/Hg_2SO_4 anode).

ACKNOWLEDGEMENT

Acknowledgement is made to the Chief Scientist, British Ministry of Supply, for permission to publish this paper.

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SUMMARY

The development of a method for the polarographic determination of manganese, copper, chromium and iron in the insoluble residue remaining after the dissolution of calcium metal is described. The base electrolyte used is sodium hydroxide and mannitol. The probable electrode reactions of the manganese and copper reductions in this medium are suggested.

RÉSUMÉ

Les auteurs décrivent une méthode de dosage polarographique du manganèse, du cuivre, du chrome et du fer dans le résidu insoluble restant après dissolution du calcium métallique. On utilise comme électrolyte de base l'hydroxyde de sodium et le mannitol. Une hypothèse est faite au sujet des réactions de réductions probables du manganèse et du cuivre.

ZUSAMMENFASSUNG

Es wird die Entwicklung einer Methode zur polarographischen Bestimmung von Mangan, Kupfer, Chrom und Eisen in den bei der Auflösung von Calciummetall unlöslich zurückbleibenden Rückständen beschrieben. Der benützte Grundelektrolyt ist Natriumhydroxyd und Mannitol. Die wahrscheinlichen Reaktionen an der Elektrode bei der Reduktion von Mangan und Kupfer in diesem Medium werden angedeutet.

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POLAROGRAPHIC DETERMINATION OF ANTIMONY IN LEAD-ANTIMONY ALLOYS

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INTRODUCTION

Early work on the determination of antimony in hydrochloric acid in the presence of lead by VON BAYERLE[1] and KALOUSEK[2] led to the conclusion that the polarograph could only be used for the qualitative detection of antimony because the results were variable and unpredictable. This was ascribed by KRAUS AND NOVAK[3] to variations in the acidity of the solutions. HOURIGAN[4] pointed out that this was not the whole truth but that variations in lead concentration even at constant acidity brought about a similar effect.

It is known that the antimonic ion is reduced in two stages, *viz*:

$$Sb^{+5} + 2\,e^- \rightarrow Sb^{+3} \quad \text{— (1)}$$
$$Sb^{+3} + 3\,e^- \rightarrow Sb^{\circ} \quad \text{— (2)}$$

This gives rise to two polarographic steps, the first of which occurs at about zero voltage and is not a satisfactory step to measure. The second occurs at about — 0.15 volts and is the step measured in this determination. With certain concentrations of lead and acid these steps approach each other and merge giving rise to erroneous readings. Although elimination of the lead overcomes this difficulty, the time required to carry out this separation greatly increases the time required for a determination.

The object of the present work was to eliminate the effect due to lead in the minimum of time.

DISCUSSION

Control by specifying limits of lead and acid concentration

The effect of lead and hydrochloric acid would be controlled if their concentrations could be laid down within limits in which the antimony step height could be measured reliably. Experiment I therefore was to find such limits, if they existed at all.

Polarograms were taken within the range 0-0.03*M* lead chloride and 2-10*M* hydrochloric acid, changes in diffusion current due to antimony at a series of points in that range were plotted to give a contour of the step height. The shape of this contour in the neighbourhood of the limits of lead chloride and hydrochloric acid described in a proposed method is the criterion of the feasibility of the method; the error will be less the flatter the curve.

Elimination of the effects of lead by the addition of an alkali chloride

The concentration of lead may affect the antimony in two ways:

(a) As a constituent of the supporting electrolyte it may act as described by VIVARRELI[5] and alter the half-wave potential of the two reduction steps unequally and therefore bring them together.

(b) By the formation of a complex such $PbSbCl_7$.

It is known that Sb^{+5} forms complexes of the type $M^{+2}[SbCl_7]$. It is proposed therefore that $PbSbCl_7$ existed in solution as follows:

$$PbCl_4^{-2} \rightarrow Pb^{+2} + 4\,Cl^- \quad (3)$$

$$Pb^{+2} + Sb^{+5} + 7\,Cl^- \rightarrow PbSbCl_7 \quad (4)$$

Further a two-step mechanism for the reduction of such a complex was suggested as follows:

$$PbSbCl_7 \xrightarrow{2\,e^-} PbCl_4^{-2} + Sb^{+3} + 3\,Cl^- \quad (5)$$

$$Sb^{+3} \xrightarrow{3\,e^-} Sb^\circ$$

The potential at which Sb^{+5} is reduced to Sb^{+3} is clearly altered by this complex formation.

It was decided to decrease the Pb^{+2} concentration by the addition of an alkali chloride thus disturbing equation (3). It would also greatly reduce the interference of lead due to both causes (a) and (b).

RESULTS

Control by specifying limits of lead and acid concentration

It can be seen from Fig. 1 that the results obtained are unsuitable for analytical purposes and that it was not found possible to prescribe satisfactory limits within which the analysis could be carried out. The figure also serves to illustrate the conditions under which the two steps merge and give very bad results, as observed by KRAUS AND NOVAK and by HOURIGAN (*loc. cit.*).

Elimination of the effects of lead by the addition of an alkali chloride

The alkali chlorides tried were those of sodium, potassium, lithium and ammonium. Preliminary experiments showed that potassium, lithium and ammonium

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chlorides were favourable, but that with sodium chloride the beginning and the end of the antimony step were rounded and therefore not easily measured. Further experiments were therefore confined to potassium chloride.

The addition of potassium chloride to the mixture giving a saturated solution caused the precipitation of lead chloride. The polarographic curves obtained were very easily measurable since the potassium chloride had the effect of flattening the step before and after the rise.

The step height was found to be proportional to the antimony concentration provided that concentrations did not exceed $0.002M$ and that the solution was in all cases saturated with potassium chloride. This included the standard solution.

Variation of pH caused slight changes in the height of the antimony step for the constant concentration. This indicated that the standard and the sample must be determined under the same conditions of molarity of hydrochloric acid.

Increase of the concentration of the antimony above $0.002M$ caused the step to break up. This effect was shown to be a feature in the presence or absence of lead and of potassium salts. See Figs. 1 and 2.

The estimation was found to be satisfactory within the range 4 to 8 molar hydrochloric acid. 0 to $0.03M$ lead and 0 to 0.002 in antimony.

The oxidation state of the antimony did not cause any alteration to the results. Solutions containing only Sb^{+5} or Sb^{+3} or a mixture of 50% Sb^{+5} and 50% Sb^{+5} gave accurate results.

Acid concentrations of less than $4M$ were not recommended in order to avoid any difficulty arising from hydrolysis of the antimony.

It is a matter of some importance to the analyst that the procedure for standardising should be as simple as possible. In fact the adoption or rejection of a particular method may well turn on this point. Tests were made to see if there was any need to include lead chloride in the standard solution. It was found that the diffusion current was the same for a given concentration of antimony under conditions with or without lead chloride when the solution was saturated with potassium chloride.

EXPERIMENTAL

Solutions

Antimony Chloride. Antimony trichloride was dissolved in concentrated hydrochloric acid and sufficient bromate was added to oxidise half of it. The solution was then made up with concentrated hydrochloric acid to give a concentration of $0.02\ M$ antimony.

Lead Chloride. $PbCl_2$ was dissolved in concentrated hydrochloric acid and made up to give a $0.1M$ solution of Pb^{+2}.

Potassium Chloride. KCl crystals were added in excess to water, giving a saturated solution.

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Gelatine. 2 g of gelatine were dissolved in a small amount of HCl. This volume was then adjusted to 100 ml.

The above were used as stock solutions. The series examined were made up by taking the required quantity of stock solution and adjusting volume.

Series examined

Several series of mixtures were made up and the antimony estimated polarographically. In all cases the antimony existed as 50% Sb^{+3} and 50% Sb^{+5}. Care must be taken with Sb^{+5} in solution when the acid is less than 4*M* since hydrolysis is liable to occur, which causes bad results.

The results are shown in Table I.

TABLE I

Sb mole/l	Pb mole/l	KCl mole/l	HCl 2*M*	HCl 5*M*	HCl 7*M*
			←	Step height	→
0.0010	Nil	Nil	14	14	15
0.0015	Nil	Nil	20	22	21
0.0020	Nil	Nil	28	31	29
0.0025	Nil	Nil	36	39x	37x
0.0030	Nil	Nil	43	46x	43x
0.0035	Nil	Nil	47	52x	50x
0.0040	Nil	Nil	54x	57x	56x

The above was then repeated with solutions saturated in potassium chloride. Results are shown in Table II.

TABLE II

Sb mole/l	Pb mole/l	KCl mole/l	HCl 2*M*	HCl 5*M*	HCl 7*M*
			←	Step height	→
0.0010	Nil	Sat	13	13	13
0.0015	Nil	Sat	19	20	19
0.0020	Nil	Sat	24	26	25
0.0025	Nil	Sat	30	32x	31x
0.0030	Nil	Sat	38	40x	40x
0.0035	Nil	Sat	42x	45x	44x
0.0040	Nil	Sat	47x	51x	50x

All step heights marked (x) were the total of two or more small steps.

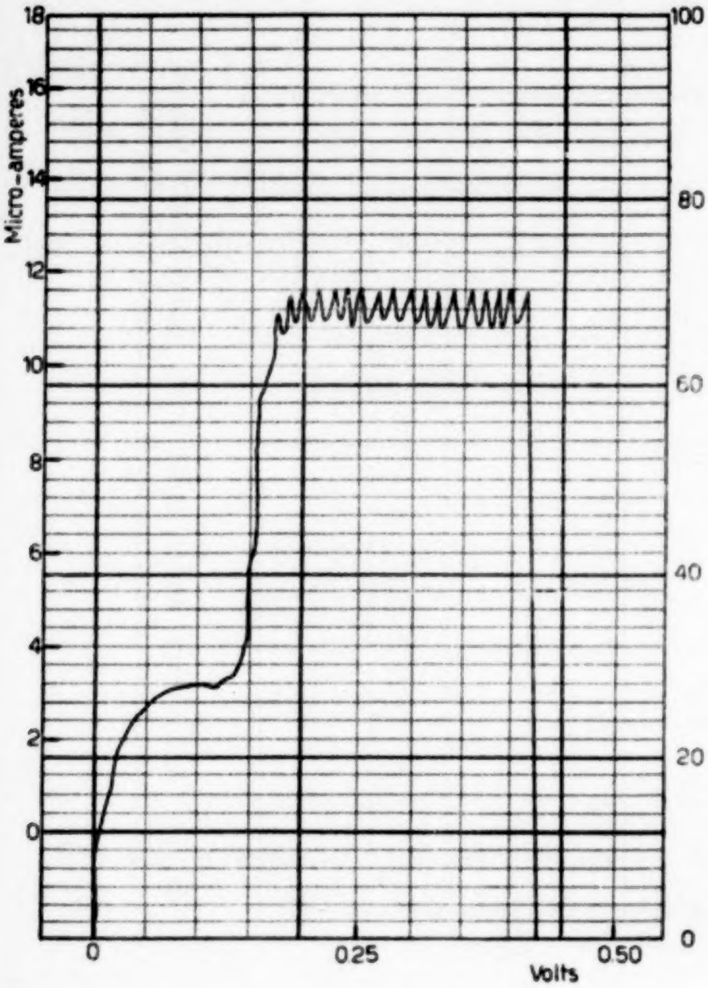

Fig. 1. Wave produced by antimony under the conditions described.

The step height of the antimony wave was found to be approximately proportional to its concentration. It was noted, however, that when the concentration exceeded 0.002M that the wave split into two small waves and that the concentration was proportional to the sum of these waves. Further increase in antimony concentration caused the wave to split into three small waves. This suggests that the antimony associates in more concentrated solutions.

The potassium had no effect on this wave splitting, but slightly decreased the step height given by a standard antimony concentration.

To avoid complications caused by the splitting of the step further experiments were carried out using a concentration of 0.002M antimony.

A series was carried out in which the antimony was maintained at 0.002M and the hydrochloric acid concentration varied. Results are shown in Table III.

TABLE III

Sb	Pb	HCl (molarity)	Step height Sat. in KCl	KCl Nil
0.002M	Nil	2	31.0	33.0
,,	,,	3	31.5	33.0
,,	,,	4	32.0	33.0
,,	,,	5	32.0	33.0
,,	,,	6	31.0	33.0
,,	,,	6.3	31.0	32.5
,,	,,	6.5	32.0	32.5
,,	,,	6.7	31.5	33.0
,,	,,	7	32.0	32.5
,,	,,	8	31.0	32.0

The effect caused by the change in hydrochloric acid concentration seemed to be small when the antimony concentration was restricted in this way.

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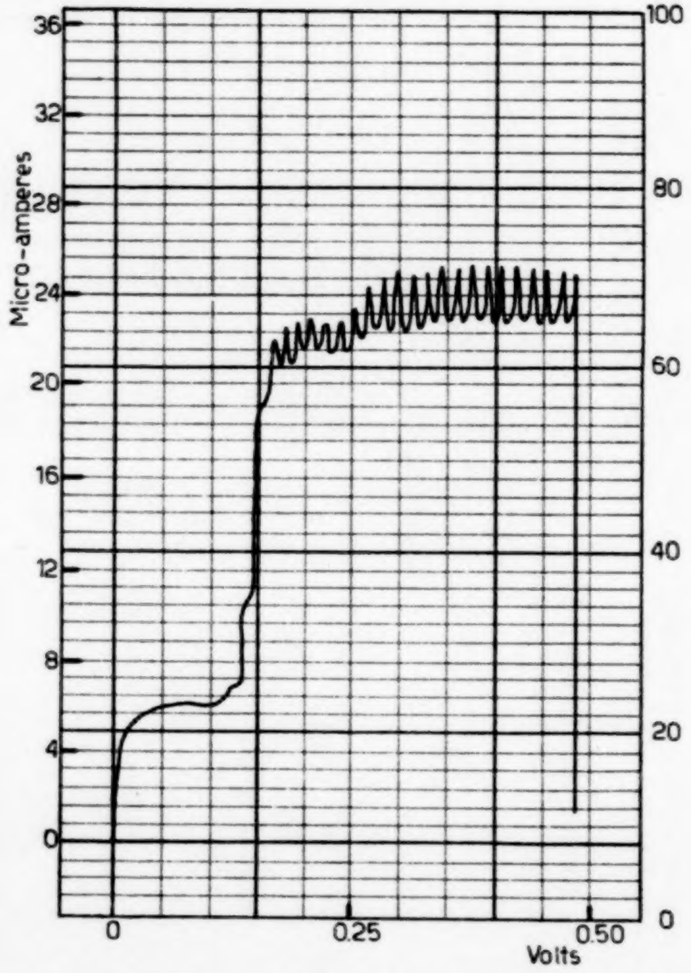

Fig. 2a. Wave split when concentration of antimony is too great.

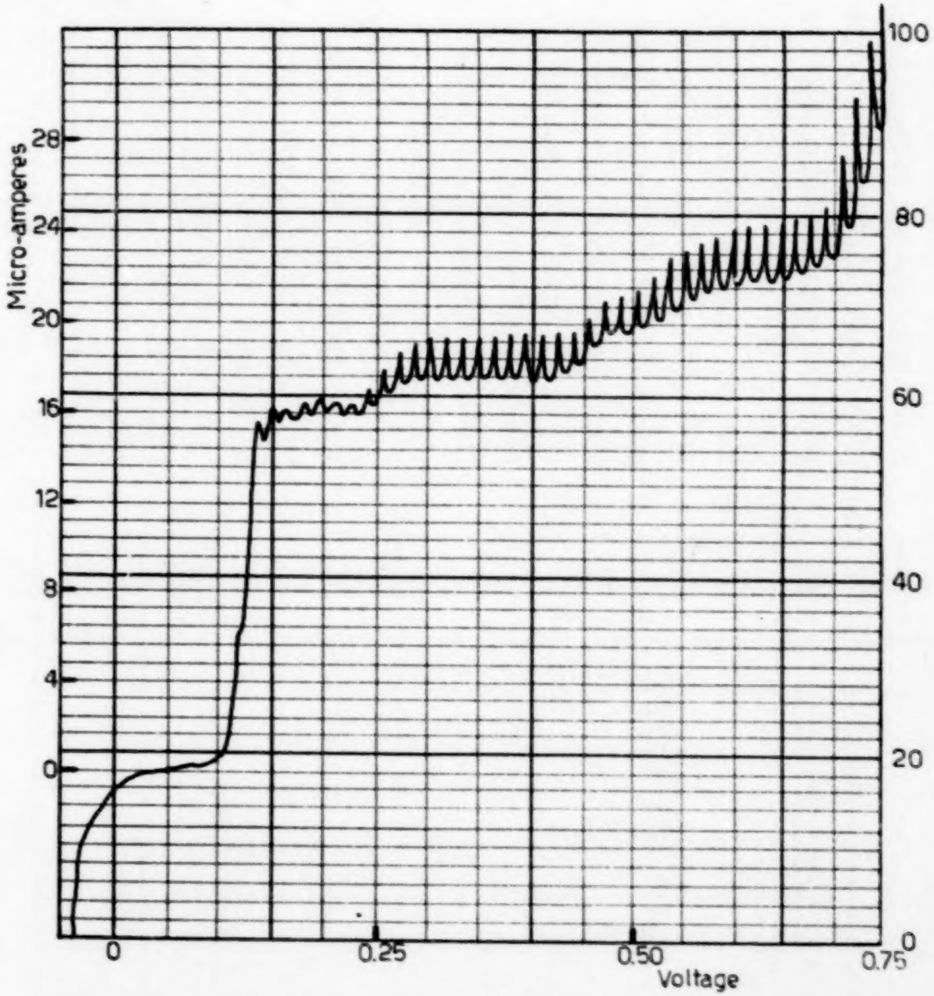

Fig. 2b. Antimony wave split into three parts when the concentration of antimony is increased still further.

Experiment I

The effect of lead, in the absence of potassium, was next examined, the following mixtures were prepared:

Molarity of lead	Molarity of antimony	Molarity of hydrochloric acid
Nil	0.002M	2M
0.0025M	,,	,,
0.005	,,	,,
0.0075	,,	,,
0.0075	,,	,,
0.010	,,	,,
0.0125	,,	,,
0.0150	,,	,,
0.0175	,,	,,
0.020	,,	,,
0.0225	,,	,,
0.025	,,	,,
0.0275	,,	,,
0.030	,,	,,

The above series was repeated with the molarities of hydrochloric acid changing to 3.4.5.6.7.8.9. molar respectively.

A summary of the step height for the antimonic wave is given in Fig. 3.

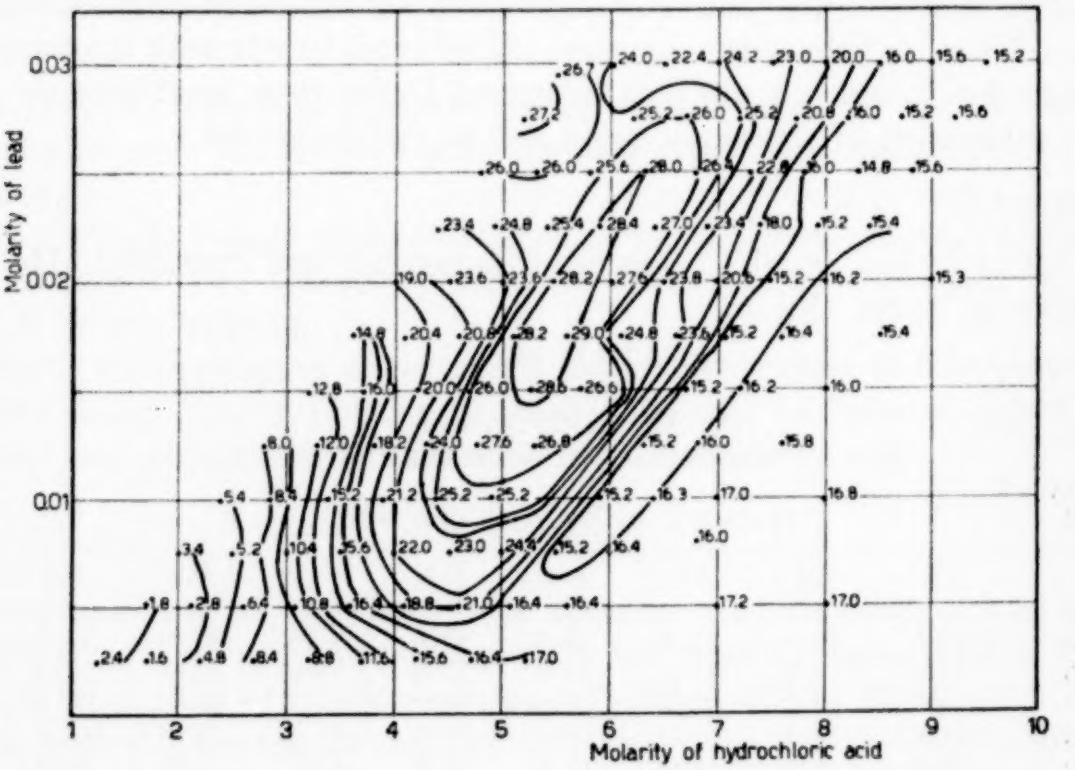

Fig. 3. Relative diffusion current of antimony(V) in the presence of lead and hydrochloric acid. Potassium absent

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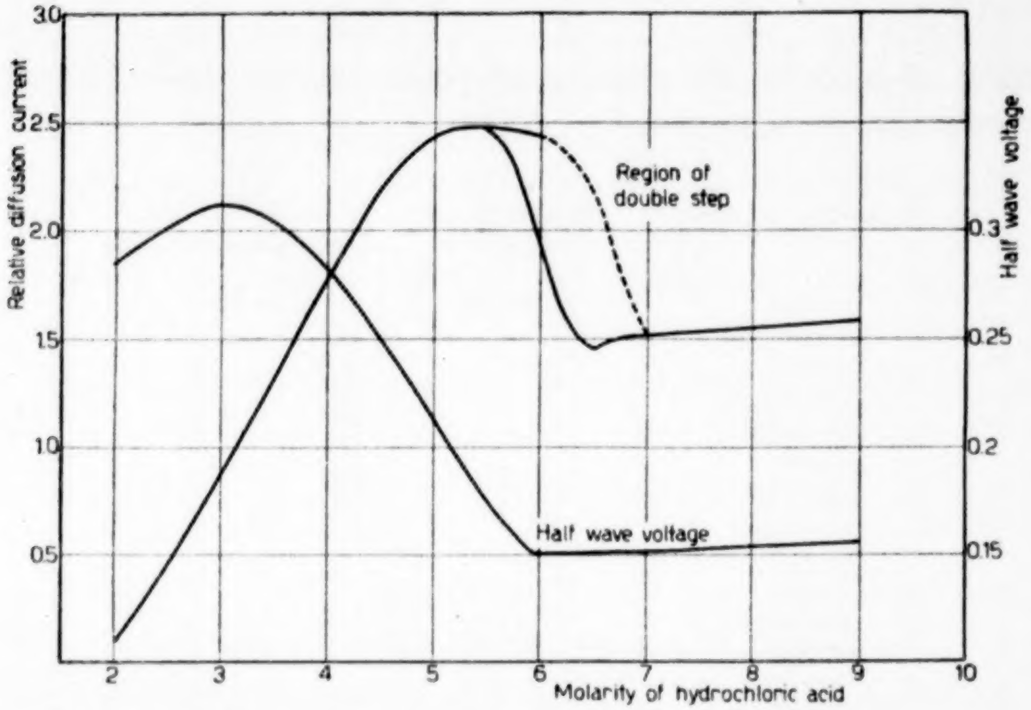

Fig. 4. Relative value of the diffusion current given by 0.002 molar antimony(V) in the presence of 0.01 *M* lead, and varying hydrochloric acid concentration.

The variation in step height when the concentration of lead was 0.01*M* is shown in Fig. 4 which also shows the voltage at which the step appeared and the region of the double step spoken of by KRAUS AND NOVAK and by HOURIGAN (*loc. cit.*).

It was shown that the antimony wave varied considerably with the composition of the solution in which it was polarographed. Under these conditions the polarographic estimation of antimony could not be recommended.

Experiment II

The effect of lead in the presence of potassium was examined. The results are shown in Table IV.

TABLE IV

Antimony 0.002*M*
Potassium chloride saturated

Molarity of lead	Molarity of hydrochloric acid								
	2.0	3.0	4.0	5.0	6.0	6.3	6.7	7.0	8.0
	Step height								
.030	25.0	30.0	31.5	31.5	31.0	31.5	31.0	31.5	31.5
.025	25.0	31.0	31.5	31.0	31.5	32.0	31.0	31.5	31.0
.020	24.0	30.5	32.0	31.5	31.0	31.0	31.5	31.5	31.0
.015	25.0	30.0	31.5	31.0	30.5	31.5	31.0	31.5	31.5
.010	25.0	31.0	31.0	31.0	31.0	32.0	32.0	31.0	31.5
.005	25.0	31.0	31.5	32.0	31.5	31.5	31.5	31.5	31.0
Nil	20.5	29.0	32.0	31.5	31.0	31.0	31.0	32.0	31.5

This was repeated with solution saturated with sodium chloride, ammonium chloride and lithium chloride respectively in 8*M* hydrochloric acid only, as shown in Table V.

TABLE V

Antimony 0.002*M*
Hydrochloric acid 8*M*
STEP HEIGHT

Molarity of Lead	Lithium chloride saturated	Ammonium chloride saturated	Sodium chloride saturated
0.030	25.0	29.5	31 Step not
0.015	25.0	29.0	32 easily
Nil	25.0	29.0	31 measurable

Results showed that the ammonium chloride and lithium chloride might be as effective as the potassium chloride but that the sodium chloride was not so effective.

In all cases the solution contained 0.2% gelatine as a maximum suppressor. The measurement of the step height is intended as a measure of diffusion current. There is no relation between the actual heights shown in different tables. Such a relationship could not be expected owing to variation in the capillaries used during the experiments.

Interferences

Tin. If appreciable quantitities of tin are present the metal must be eliminated from solution since tin gives an indeterminate step which invalidates the step by antimony.

Copper. Cupric copper gives two steps under these conditions, the second of which is close to the antimony step. Its effect can be eliminated by adding E.D.T.A. to the solution.

Bismuth. Bismuth gives a step which appears very close to that produced by antimony under these conditions. If present, it must be removed before polarographing, any present will be included in the antimony step.

CONCLUSION

The method evolved was found to be accurate over the range of lead and acid concentrations described and quite suitable for routine purposes. After the alloy was in solution, the estimation can be completed within thirty minutes.

The accuracy of the results could be depended upon to within 0.02% in an alloy containing 1% antimony. This is within the limits of accuracy of the polarograph.

RECOMMENDED PROCEDURE

Procedure used for alloy containing 0.8% antimony in lead.

Reagents

Hydrochloric acid	a) concentrated b) 5 molar
Bromine (liquid)	
Hydrogen peroxide	20 vols.
Gelatine maximum suppressor	0.8 Gelatine in 100 ml 10 molar hydrochloric acid
Potassium chloride —	Saturated solution
Standard antimony solution —	0.5336 g Potassium antimony tartrate (AR. dissolved in 5*M* hydrochloric acid 100 ml contained 0.2 g antimony)

Method

0.25 g of lead-antimony alloy was rolled down to a fine gauge 0.002″ and then dissolved without boiling in concentrated hydrochloric acid 15 ml containing liquid bromine (1 ml).

When completely dissolved, hydrogen peroxide (2.5 ml) was added and the mixture boiled. Any bromide present was thus oxidised by the hydrogen peroxide to bromine, and boiled off with the excess bromine. The volume of the solution was then reduced by boiling until lead chloride started to crystallize out.

After cooling, the solution was transferred to a 25 ml standard flask containing 4 ml of potassium chloride solution. The beaker was washed out with 6.5 ml of gelatine solution and successive washes of 5 molar hydrochloric acid. All washings were added to the standard flask until the required volume had been reached.

The solution was shaken and cooled to 20° C, the volume being adjusted if necessary with 5*M* hydrochloric acid. After settling the supernatant solution was pipetted into the polarographic cell and the second polarographic antimony step determined.

A standard solution was made up by first dissolving 0.5 g of pure lead in hydrochloric acid and bromine and then adding 2 ml of standard antimony solution.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Dr. W. G. Radley, E-in-C, G.P.O, for permission to publish this work. Also to Messrs. C. Elliott and N. Wild B.Sc., who carried out much of the experimental work.

SUMMARY

A polarographic method for the determination of antimony in lead-antimony alloys has been developed. It was found that the interference due to the presence

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of varying concentrations of lead and hydrochloric acid would be eliminated by the addition of potassium chloride.

The method gave satisfactory results within the range:

Hydrochloric acid	4 — 8*M*
Lead	0 — 0.03*M*
Antimony	0 — 0.002*M*

Within the limits described, the antimony concentration was found to be proportional to the height of the antimony step with a half-wave voltage of approximately — 0.15 V *i.e.* the Sb^{+3}/Sb amalgam step. This was independent of the state of oxidation of the antimony. It was found necessary to carry out the standardisation at the same molarity of hydrochloric acid as the test sample.

Preliminary tests with ammonium chloride and lithium chloride showed that they gave similar results to potassium chloride but sodium chloride was less suitable.

RÉSUMÉ

Une méthode polarographie pour le dosage de l'antimoine est appliquèe aux alliages plomb-antimoine. Les perturbations causées par la présence du plomb et de l'acide chlorhydrique, en concentrations variables, sont éliminées par addition de chlorure de potassium.

La méthode donne des résultats satisfaisants pour les concentrations suivantes:

Acide chlorhydrique	4 — 8*M*
Plomb	0 — 0.03*M*
Antimoine	0 — 0.002*M*

Dans ces limites, la hauteur du saut de l'antimoine est proportionnelle à sa concentration; le potentiel de demi-vague est d'environ —0.15 V (Sb^{+3}/Sb amalgame). Il est indépendant du degré d'oxydation de l'antimoine. D'autre part, il est nécessaire que la concentration de l'acide chlorhydrique soit toujours la même, pour l'étalonnage et pour l'analyse.

Des essais préliminaires ont été effectués avec le chlorure d'ammonium et le chlorure de lithium; ils donnent les mêmes résultats que le chlorure de potassium; par contre, le chlorure de sodium convient moins bien.

ZUSAMMENFASSUNG

Es wurde eine polarographische Methode zur Bestimmung von Antimon in Blei-Antimon-Legierungen entwickelt. Es wurde gefunden, dass die Störung, die der Anwesenheit von wechselnden Konzentrationen von Blei und Salzsäure zuzuschreiben ist, durch Zusatz von KCl elimiert werden kann.

Die Methode ergab in dem Bereich von 4—8*M* Salzsäure, 0—0.03*M* Blei und 0 — 0.002*M* Antimon befriedigende Ergebnisse.

Es wurde gefunden, dass innerhalb der beschriebenen Grenzen die Antimonkonzentration proportional zur Höhe der Antimonstufe mit einer Halbstufen potential von ungefähr —0.15 V war, d.i. die Sb^{+3}/Sb-Amalgam Stufe.

Dies war unabhängig von der Oxydationsstufe des Antimons. Es war nötig, wie gefunden wurde, die Eichung bei der gleichen Salzsäurekonzentration auszuführen wie die Vergleichsprobe.

Vorläufige Untersuchungen mit Ammoniumchlorid und Lithiumchlorid ergaben ähnliche Werte wie Kaliumchlorid. Natriumchlorid jedoch erwies sich als weniger geeignet.

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SPECTROCHEMICAL ANALYSIS IN METALLURGY

by

J. B. GILLIS (GHENT)

Report of the O.E.C.E. — Mission no. 80 — at the First World Metallurgical Congress 1951

Analytical chemistry in metallurgy has taken entirely new aspects since the last world war.

Applied spectrochemistry enables the metallurgist to know the composition of his alloys, in a fascinating short time. One or two minutes are sufficient, with direct-reading instruments, to obtain the analytical result by means of emission-spectrochemical methods. It is no longer necessary to make solutions of the alloy in question and to operate in the wet way using classical methods or colorimetric procedures improved by absorption spectrophotometry. Much easier and faster are the instrumental methods, where light is emitted by a spark or arc produced between electrodes, one of them being the alloy to be analysed, and, where, for each element, the intensity of the emitted light is converted into a corresponding amount of electricity by means of photoelectrical devices.

In the great majority of the research laboratories and institutes visited by group 8 B, the members of the group were able to see these direct-reading instruments in action and to observe the revolutionary change of the analytical methods used in metallurgy. One can say just like CHESTER M. ALTER in the "Symposium on Economic Aspects of Chemical Analysis in Manufacturing" at the Diamond Jubilee Meeting of the American Chemical Society, that this new situation and the tremendous development of instrumental methods in modern analytical chemistry makes necessary a complete renewal of chemical education and of scope of analytical curriculum for those who have to be prepared for their adequate role in metallurgy.

The precision of direct analysis is excellent. As an indication, the current error on a series of analysis is generally around 1% of the content. It is necessary to operate in a conditioned room.

The adjustment of direct-reading spectrometers is always rather long and may easily require one full month, even for a specialist. This time may possibly be shorter in the United States thanks to the cooperation of field engineers from the manufacturer.

The adjustment should always be made according to the mean content of analysed alloys. When this content varies over a rather wide range, it may be necessary to choose different analysis bands for the various concentration fields. As a consequence, the instruments with a considerable number of photoelectric cells naturally offer wider possibilities.

We were told that the latest models of A.R.L. quantometers are fitted with a rating valve, thanks to which constant predetermined quantities of energy may be sent through the various outlet slits, avoiding the frequent rating of the instrument with reference samples, but it is not yet possible to form a judgment as to the value of this device.

The members of group 8 B, visiting the research laboratories of Aluminium Company of America at New-Kensington (Penn.) were received by Dr. J. CHURCHILL Jr. in the spectrochemical department, who explained to them how the photoelectronic analysis of aluminium and alloys can be realised with the quantometer, a direct-reading spectrometer of great speed and accuracy, representing an outstanding achievement in metallurgical control. He presented the first quantometer delivered by A.R.L. and working with only 12 receivers, then a later model permitting the determination of all usual elements and finally the latest model with standardisation lamp. At that time 13 quantometers were in use in the plants of the Alcoa, installed for the complete control of production of aluminium.

In the factories, the total analysis time does not exceed 4 minutes, including the preparation of samples. All usual elements may be titrated by the spectrochemical method, including Si up to 15% and Cu up to 30% (except perhaps in the difficult case of duralumin class of alloys, for which sufficiently accurate data could not be collected).

The direct spectrochemical analysis allows the rapid correction of the load during the smelting and consequently the use of relatively high proportions of scrap.

The production of magnesium at Dow Chemical Co. in Midland (Mich.) is entirely controlled by direct-reading equipment, constructed by Baird Associates. Complete analysis of complex magnesium alloys are obtained by push button operation, clock dials giving directly the per cent. composition in a matter of one minute. This means an increased furnace production of critical materials and an assistance in scientific research.

Analogous instruments as for the aluminium and the magnesium industries are in use in steel producing companies, eight to ten usual chemical elements being measured simultaneously, results being comparable and in many cases superior to chemical analysis in accuracy.

The members of the steelmaking and refining group were able to see those control instruments in operation in different steel plants near Detroit and were impressed by the speed and accuracy that they insure for high quality metallurgical production.

It should be noted that the boron content of steel is easily measured to about 0.001% by the methods applied to minor elements, as is confirmed by the Belgian experience.

For phosphorus, measurement methods have been developed in the United States and in Belgium, namely by WOLFE at Ann Arbor, Michigan, by HANS at Liège and BRECKPOT at Louvain.

The measurements of oxygen and nitrogen are still in the experimental stage and, as far as we know, no industrial process is in existence, either in the United States or in Europe.

In the different research laboratories visited by the Group, complete units for spectrochemical analysis were in use ensuring qualitative and quantitative analysis of metals, alloys and materials with metal or metalloid constituents, some metalloidic components escaping to their spectrographic detection. Those units comprise generally a spectrograph of sufficient resolution, an excitation unit, a microphotometer, photographic processor and appropriate calculator.

In the institutions under direct Government control the National Bureau of Standards and the United States Navy Research Laboratories have a good spectrochemical equipment. In the N.B.S. Dr. W. BRODE AND Dr. B. SCRIBNER are well-known authorities in applied chemical spectroscopy. They gather and publish with Dr. W. F. MEGGERS, an index of the literature on spectrochemical analysis and, with the A.S.T.M., procedures on spectrochemical methods. Dr. B. F. SCRIBNER is working on testing steel standards, stainless steel and alloy tool steels. He has also a Baird direct-reading spectrometer at his disposal for rapid testing of standard samples of steel for homogeneity.

In the United States Navy Research Laboratories spectrochemistry was applied to the production of very pure metals and on improving techniques for chemical analysis. M. B. CAVANAGH worked on tin standards and on aluminium in a nitrogen atmosphere, making use of a Baird 3 M Grating Spectrograph, permitting the utilisation of a rotating sector before the slit. He attempted also the determination of sulfur and selenium in steel by heating material by induction, a method quite analogous to that of GATTERER for the detection of metalloidic constituents.

Research institutions attached to a University were also engaged in spectrochemical analysis and techniques.

The Institute for the Study of Metals (Chicago University) has a spectrochemical department placed under the direction of Dr. N. H. NACHTRIEB, author of a well-known book: "Principles and practice of spectrochemical analysis". Spectrochemical problems concerned with the study of metals and the solid state are solved there by means of a complete unit for spectrographic analysis.

The University of Michigan has fine equipment for spectrochemical analysis in the Department of Physics (Dean: Dr. BARKER). A course of applied spectroscopy is given there by Dr. R. A. WOLFE consisting of two lectures a week on equipment and methods of spectrochemical analysis with laboratory practice during one or two afternoons. Dr. WOLFE is an authority on questions concerning controlled spark circuits using air interrupter, with trace analysis in iron and steel and on the use of multiplier phototubes or Geiger-Müller photoelectron counters in the determination of phosphorus and steel. Researches done in this laboratory were fundamental for the realisation of the Leeds & Northrup spark discharge source and the Spec-Power Console Cabinet of the National Spectrographic Laboratories.

Applied Research Institutions: Mellon Institute (Pittsburg) and Battelle Memorial Institute (Columbus), visited by group 8 B, were also of interest for their spectrochemical achievements.

Dr. EDWIN S. HODGE received the conferees in the spectrochemical department of the Mellon Institute. He explained that this department deals with the analytical problems presented by the fellows connected with the Institute. It operates with a 2 M-A.R.L. grating spectrograph, and infrared recording spectrophotometer, a Bausch & Lomb Medium Quartz-Spectrograph equipped for Raman-spectroscopy and a Beckman flame-photometer.

Industrial laboratories and pilot plants were in general equipped with modern spectrochemical apparatus which give outstanding services to the rapid development of new achievements.

The Bell Telephone Co. (Murray Hill, N.Y.), reducing fundamental research to practical applicable ideas, has a chemical department placed under direction of Dr. R. M. BURNS. Dr. JAYCOX is head of the spectrochemical division, working with a Jarrell-Ash 3 M-Grating Spectrograph and a N.S.L. Spec-Power source unit. His work is concerned with the analysis of new materials and substitution work for material critical in wartime. Dr. J. A. BURTON was using isotopes for the analysis of antimony in germanium by the same method applied by Dr. J. H. HIPLE, in 1951, in the atomic physical section, for the analysis of stainless steels for Cr and Ni. Dr. N. B. HANNAY was concerned with mass-spectrography of solid substances, an entirely new subject of investigations. It is obvious that the chemical department of the Bell Telephone Research Laboratories is able to study the numerous metals and alloys that compose the Bell Telephone plant and that good ideas are giving the ideal impulse to first class realisations. Reprints of papers given by personnel of the Bell Telephone System can be obtained free of charge.

The United States Steel Corporation at Pittsburgh is another example of a plant having a complete spectrographic unit equipped with A.R.L. 2 M-Grating Spectrograph and accessories. Dr. MICHAELIS AND Dr. G. E. PELISSIER received the conferees and explained their work on spectrochemical analysis of steel and refractories and their investigations on standards for tin coating (tin on iron plate). They also stated that the Fisher Co. at Pittsburgh was studying a new direct-reading instrument for spectrochemical analysis of steel.

International Harvester (Chicago) has a physical laboratory under the direction of Dr. ELLIS, including a spectrochemical division of particular interest for the conferees. It operates with a 2 M-Grating Spectrograph, Multisource and densitometer A.R.L., studying procedures to be used in the plants, where seven of these equipments are daily in action. Apart from these instruments International Harvester has one quantometer (1.5 M-Grating) in its steel work.

Chrysler Corporation (Detroit) is equipped with a complete N.S.L. Spec-Power Unit for spectrographic analysis, a Bausch & Lomb Medium and a Littrow Spectograph, an A.R.L. Densitometer and a photographic room. Being also an engineering school delivering grades and doctors degrees in engineering, the spectrochemical division operates as an education centre. The conferees were received in the division by GORDON ADAMS, working there for his Bachelor degree.

General Motors Corporation (Detroit), Ford Motor Co. (Detroit), Carnegie Illinois Steel Co. (Homestead), Bethlehem Steel Co. (Bethlehem), Rotary Electric Steel Co.

(Detroit), MacLouth Steel Co. (Trenton), etc. have in their plants spectrographic units or direct-reading instruments. The same can be said for the non-ferrous metal fabrication in the United States; the Titan Mills, for instance, have installed the new quantometer for the complete analysis of brass or bronze alloy, for the selection of raw materials and for the control of brass products.

It is clear that Europe has to follow the example and to make use of direct-reading spectrographic instruments in its metallurgic production. In Belgium and in France automatic direct-reading instruments were conceived and realised; in Sweden, too for analysis of solutions. Other countries in the World will also undoubtedly substitute instrumental methods of analysis to their normal chemical procedures.

One of the most important achievements of the Technical Assistance Mission No. 80 may be noted as the revelation, for most of the conferees, of the new realisations in the domain of instrumental analytical chemistry and, more specially, of the spectrochemical methods applied to practical metallurgy.

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BOOK REVIEWS

Tables of Percentage Composition of Organic Compounds, by H. GYSEL, Birkhäuser, Basel, 1951, 637 pp., 125.— Swiss francs.

This book meets an obvious demand. In spite of the tremendous progress in the application of spectroscopic, polarographic, and other physicochemical methods to the identification of new organic compounds, the elementary percentage compostion as determined by quantitative chemical microanalysis still forms the soundest basis of any rigorous proof of structure. A large number of chemists concerned with percentage composition will no doubt adopt Dr. GYSEL's book for their everyday work on this account.

The book includes the following items: Percentage tables of the atoms in organic compounds of types C — H from C_1H_4 to $C_{60}H_{122}$; types C — H —O ($C_1H_2O_1$ — $C_{52}H_{106}O_6$); types C — H — N ($C_1H_1N_1$ — $C_{50}H_{60}N_6$); and types C — H — O — N ($C_1H_1O_1N_1$ — $C_{50}H_{102}O_4N_6$); International Atomic Weights; a table with multiples of molecular weights of elements and organic groups: Supplementary tables for the determination of nitrogen according to the gas volumetric method: and, finally, a Condensed Table of four place logarithms. Furthermore the book suggests a simple arithmetic rule which permits the Tables also to be used for compounds containing sulphur since the atomic weight of sulphur is practically double that of oxygen. The author states in the preface that all the calculations had been checked several times and by different methods and that therefore the table should be almost free from errors. The reviewer has checked a number of the figures on different occasions without encountering a single deviation.

This book will be highly welcomed by all those who heretofore had to make percentage calculations themselves and who are therefore going to be relieved from a time-consuming routine job.

The high price of the book will keep many individual workers from buying it but appears fully justified considering the effort involved in producing it and the time it may save particularly in large departments.

Dr. GYSEL's *Tables* will prove a useful tool to all workers in the fields of organic microanalysis, advanced organic research, and literature or patent survey. The author is to be congratulated on the unselfish and unrewarding task he has undertaken for the benefit of many others.

MAX ROTTENBERG (Geneva)

Kolloidchemisches Taschenbuch, von ALFRED KUHN unter Mitwirkung zahlreicher Fachgenossen, 4. Auflage, Akademische Verlagsgesellschaft, Geest & Portig K.G., Leipzig, 1953. Volume relié de 519 pages et 143 figures, D.M. 24.—.

Ce livre ne s'adressant pas exclusivement au spécialiste en chimie des colloïdes, qu'il me soit permis d'en donner une récension en considérant le point de vue du chimiste non spécialisé.

Cet ouvrage est le résultat de la collaboration d'une vingtaine de spécialistes, dont plusieurs de grande réputation. On peut donc considirer les données comme dignes de confiance, ce qui est d'une grande importance pour les lecteurs non spécialisés.

Il couvre pratiquement tout le domaine de la chimie des colloïdes: la systématique, la préparation et la stabilité, la cinétique, le mouvement brownien, la sédimentation, l'osmose et la diffusion, la dialyse, l'ultrafiltration et l'électrodialyse, la coagulation, la mesure des poudres fines, l'optique, y compris l'analyse par rayons-X et la microphotographie électronique, la tension superficielle, la viscosité, les couches monomoléculaires, l'adsorption, le comportement électrique, les gels, etc. etc. On nous en présente les notions fondamentales théoriques, les formules, les appareils de mesure et quelques résultats.

L'étendue du livre, déjà assez considérable, a obligé les auteurs à passer sous silence un certain nombre de sujets pratiques, comme par exemple la chromatographie.

Ce livre sera très utile à tous les chercheurs non spécialisés qui sont obligés de se mettre au courant de quelque domaine de la chimie des colloïdes et rendra également certainement des services aux chercheurs en chimie des colloïdes.

C. J. VAN NIEUWENBURG (Delft)

Lehrbuch der organischen Chemie (in drei Bänden) von F. KLAGES. Walter de Gruyter & Co. Berlin, 1953. 1 Band, 2 Hälfte: 543 Seiten, 5 Abb., 16 Tab. Ganzl. DM 62.—.

Nous avons déjà eu l'avantage de présenter à nos lecteurs le premier volume du remarquable Traité de Chimie Organique du Prof. F. KLAGES *(cf. Anal. Chim. Acta*, 7 (1952) 594). Un certain retard étant survenu à l'édition, le plan primitif de parution a dû être quelque peu allongé et ce n'est que ce jour que nous recevons le deuxième volume de la série.

Terminant la partie descriptive de ce que nous pourrions appeler la chimie organique systématique, ce volume présente les mêmes caractéristiques de clarté et d'intelligente exposition du sujet qui nous avaient séduits dans le premier tome. Il convient d'autre part de noter un point qui ressort de la lecture de l'ensemble de cette première partie: l'ampleur même de l'ouvrage permet à l'auteur de traiter son sujet avec sensiblement plus de détails — souvent exposés comme cas particuliers illustrant certaines propriétés générales — que ce n'est généralement le cas dans des ouvrages de ce genre. C'est dire que si ce traité est destiné avant tout aux étudiants en chimie, il sera également précieux aux chimistes avertis qui y trouveront souvent tel renseignement désiré, sans avoir besoin de recourir à la littérature spécialisée.

Un bref extrait de la table des matières donnera une idée du champ couvert par ce deuxième volume:

chapitre 6: composés de l'azote.
chapitre 7: composés du soufre.
chapitre 8: composés organiques contenant des éléments non-métalliques.
chapitre 9: composés organométalliques.
chapitre 10: composés à fonctions anormales.
chapitre 11: composés cycliques et hétérocycliques.
chapitre 12: réactions du carbone: réaction d'oxydation, de réduction, formation et scission des liaisons entre carbones.

Nous rappellerons enfin que, des 2 volumes encore à paraître, le premier traitera des bases théoriques de la chimie organique, alors que le dernier passera en revue certains chapitres importants tels que les colorants, les sucres, les acides aminés, etc.

G. BARBEZAT (Genève)

Chimie Analytique appliquée à la Métallurgie par M. HUYBRECHTS, 3ème Edition, publiée par R. CHANDELLE ET C. VANDAEL, 472 pages, Editeurs Masson & Cie Paris, 1953, et Sciences et Lettres, Liège, Fr. Belges: 400.—.

Cette nouvelle édition, considérablement augmentée, comprend un grand nombre de méthodes de dosages en usage dans l'industrie. Les auteurs en ont fait un choix judicieux et n'ont retenu que des dosages contrôlés et parfaitement mis au point. On y trouve aussi, clairement exposées, les bases théoriques sur lesquelles repose chaque détermination.

Ce livre est fort bien présenté et renferme un grand nombre de figures particulièrement soignées.

Parmi les nombreux chapitres que comprend cet ouvrage, citons ceux qui traitent du dosage des minerais de fer, de manganèse, de zinc, de plomb, de cuivre et d'étain. Un chapitre est réservé à l'analyse du titane et un autre à celle des eaux. Signalons aussi le dosage de l'or par voie sèche dans différentes espèces de minerais.

Enfin on trouve un important chapitre sur la spectrophotométrie, avec le mode d'emploi détaillé d'un colorimètre industriel, un exposé théorique de l'électrotitration et une description de l'appareillage.

On pourrait reprocher aux auteurs de ne pas avoir mentionné l'électrode de verre qui de nos jours est universellement adoptée.

Cette nouvelle édition rendra, nous en sommes certains, de grands services aux chimistes et à tous ceux qui s'intéressent aux méthodes de dosage en usage dans l'industrie métallurgique.

D. MONNIER (Genève)

Industrial Inorganic Analysis by ROLAND S. YOUNG, (International Nickel Co. of Canada, Ltd., New York). Chapman & Hall, London, 1953, 368 pages, 12 Diagrams, 36*s*.

The scope of the book is not as wide as might be inferred from the title. The author expresses the hope that the book will be of value to chemists in all inorganic chemical industries; nevertheless, the reader is left in no doubt that it is compiled by one whose interest and experience lie essentially in the mining and metallurgical field.

The book describes methods for the determination of about 42 elements, from aluminium to zirconium, almost all of them metals, and for the analysis of a few miscellaneous items, *e.g.* water, gases and xanthates.

For each element there is given first a useful general description of the occurrence of the element, and the methods available for its determination, including separation from interfering substances. There is then a description of the "general procedures", followed in most cases by "special procedures". The latter deal with application to particular substances containing the element, or with alternative and more modern methods, *e.g.* emission spectrographic, which are given mostly only in brief outline or merely as references to the literature.

The "general procedures" are given with adequate detail and, for the most part, appear to be the ones selected by the author from extensive personal experience. This, no doubt, explains why in general the methods are based on the well known "classical" ones. Very little use is made of modern techniques, for example, potentiometric and amperometric titrations, flame photometry, organic reagent-solvent

extraction methods, chromatography or of titrations of metals such as calcium, magnesium, nickel and zinc by the complexone procedures initiated by SCHWARZENBACH (apart from the determination of hardness in water). Not much use is made of absorptiometric ("colorimetric") methods. Micro- or semi-micro methods are not included (the reader is, however, referred to the books of EMICH AND SCHNEIDER and of BENEDETTI-PICHLER).

The book will, no doubt, be useful to students and young chemists, particularly in the mining and metallurgical industries, as being a convenient source of well-tried methods.

N. STRAFFORD (Manchester)

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the Scottish Section

An Ordinary Meeting of the Scottish Section of the Society of Public Analysts and Other Analytical Chemists was held at 7.15 p.m. on Tuesday, November 10th, 1953, in the Central Station Hotel, Glasgow, when the following papers were presented and discussed:

Rapid Determination of Glycerol in Fermentation Solutions: A New Chromatographic Procedure, by K. SPOREK, M.A., and A. F. WILLIAMS, B.Sc., F.R.I.C.

A new chromatographic procedure was described for the rapid determination of glycerol in its mixtures with sugars and the constituents of molasses. It has been applied to the analysis of fermentation solutions derived from molasses. Alumina is used as adsorbent in conjunction with a solvent consisting of acetone containing 5 per cent. (v/v) water and 0.05 per cent. (v/v) glacial acetic acid. Sodium sulphite and sodium acetate are added to the sample solution to assist in the retention of sugars by the adsorbent. Glycerol is then determined in the column eluate after removal of the solvent, by direct titration of the formic acid produced after oxidation with sodium metaperiodate.

Field Analysis in Connection with Water Treatment Problems, by I. A. HEALD, B.Sc.

The paper indicates the role of field analysis and mentions some special factors which govern the choice of analytical methods. Some interesting methods, including the recently developed E.D.T.A. methods for the determination of hardness, were discussed. Examples of portable test kits were shown.

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, December 2nd, 1953, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London W.1. Dr. D. W. KENT-JONES, President of the Society, was in the Chair, and a Lecture on *Recent Advances in Medical Chemistry* was given by Professor C. H. GRAY, M.D., D.Sc., M.R.C.P., F.R.I.C., and was illustrated by lantern slides and exhibits. A discussion followed.

Synopsis of Lecture

The major advances that have recently been made in medical chemistry have been concerned with knowledge of electrolyte and water balance, of metabolic diseases such as the porphyrias, of the distribution of the serum proteins in disease, and of the exact nature of hormones and their metabolites. In this last field particularly, a more critical assessment of the role of the endocrine organs in disease has been made possible.

These advances have occurred partly because of improvements in techniques brought about by the commercial production of good physical instruments. There are a number of first class spectrophotometers for the visible, infra-red and ultraviolet parts of the spectrum, as well as good flame photometers for the determination of sodium and potassium in body fluids by emission spectrophotometry. The inadequacy of many of the commercial fluorimeters has prevented fluorescence from receiving wide application, but more recently instruments incorporating photomultiplier cells of very great sensitivity have become available and may widen the application of this analytical technique. Fractionation of serum proteins by electrophoresis on the microscale is possible, and the filter-paper technique is sufficiently simple to require a minimum of equipment. Equally striking advances in medical chemistry have been made possible by the development of chromatography and by the widespread use of isotopes. In general, however, the development of methods in medical chemistry is further advanced than is their clinical application.

THE SOCIETY FOR ANALYTICAL CHEMISTRY

(FORMERLY THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS)

At an Extraordinary General Meeting of the Society, held in London on December 17th, 1953, the name of the Society was changed to THE SOCIETY FOR ANALYTICAL CHEMISTRY.

The Society of Public Analysts was founded at a meeting held on August 7th, 1874. Membership was then restricted to practising public analysts and their assistants, but in course of time analytical chemists other than public analysts were also admitted as members. When, on August 7th, 1907, the Society was incorporated, its extended membership was recognised by the adoption of the title "The Society of Public Analysts and Other Analytical Chemists".

Even then there were doubts about the suitability of this title, and today the Society has far outgrown its original purpose of looking after the professional needs of the public analysts. The continued growth of the Society and the varied interests of its members have convinced the Council that its functions in the matter of the professional needs of analysts would be very much better discharged by the newly formed "Association of Public Analysts" and the Royal Institute of Chemistry. The new Professional Association is receiving the full support of our Society, and financial and other help has been extended to them.

The spirit of the Society has not changed, but there is no doubt that the quarters into which its interest has been directed have been altered. The developments in analytical chemistry have been so vast and striking in this period that the Society has had to grow in order to accommodate them. The inevitable feeling of regret at losing the words "Public Analysts" from the title of the Society after so many years will be softened by the knowledge that the public analysts themselves will still be with us. Whilst the Society's interest extends over the whole range of natural and manufactured products, there will still be the same platform for the discussion of investigations into the composition of food and drugs.

The Council has for some time past considered the needs of young chemists and, with the object of encouraging them, a class of Junior Membership has been instituted for chemists aged between 18 and 27 years. Junior Members will pay a considerably reduced subscription and no entrance fee, and will receive *The Analyst*. It is hoped that they will attend meetings.

There is every intention that the character of *The Analyst* and of the ordinary meetings of the Society will be maintained unchanged. The Society for Analytical Chemistry will continue in the tradition, assisting and extending the knowledge and study of all questions relating to the analysis, nature and composition of natural and manufactured materials generally.

Joint meeting of the Society for Analytical Chemistry and the Royal Institute of Chemistry

on

THE DETERMINATION OF ALCOHOL IN BLOOD AND URINE

A joint Meeting of the Society for Analytical Chemistry and the Royal Institute of Chemistry was held at 6 p.m. on Wednesday, January 20th, 1954, in the Lecture Theatre of the Institution of Electrical Engineers, Savoy Place, Victoria Embankment, London, W.C. 2. The Chair was taken by Sir HARRY JEPHCOTT, M.Sc., Ph.C., F.R.I.C., President of the Royal Institute of Chemistry, and the meeting was very well attended.

A Report on *The Determination of Alcohol in Blood and Urine* has been presented by a Panel of Analysts appointed by the Royal Institute of Chemistry to assist the Alcohol and Road Accidents Committee of the British Medical Association in the preparation of their Report on *Recognition of Intoxication*, which will be published in the course of the next few weeks. The panel consisted of Dr. D. W. KENT-JONES (Chairman), Mr. N. HERON, Mr. J. KING, Dr. R. F. MILTON, Mr. L. C. NICKOLLS and Mr. GEORGE TAYLOR, and it had the much valued advice and help of Dr. F. E. CAMPS, Dr. R. D. SUMMERS, Dr. J. B. FIRTH, Mr. E. B. PARKES and Dr. E. C. WOOD.

At the meeting Dr. D. W. KENT-JONES and Mr. G. TAYLOR presented a Survey of the Report, restricting their remarks to that portion of the Report which actually dealt wit the recommended analytical procedures, which were very carefully and specifically laid down. The methods recommended, which are: (1) an amended CAVETT micro method and (2) the macro method of KOZELKA and HINE, were discussed in particular. A satistical examination of the analytical results obtained in the final collaborative tests was also given.

Portions of the report of the Panel to the B.M.A. which dealt with translation of results from milligrams per 100 ml to amount of drink taken were not included, as they will appear in their proper context in the B.M.A.'s. forthcoming publication, *Recognition of Intoxication.*

A long and interesting discussion on the advantages and disadvantages of the methods followed, in which Sir HARRY JEPHCOTT, Dr. E. C. WOOD, Professor E. J. KING, Dr. D. I. COOMBER, Mr. H. E. MONK, Mr. A. L. BACHARACH, Dr. J. B. FIRTH and most of the members of the Panel took part.

MERCUROUS SALTS AS REDUCTIMETRIC REAGENTS FOR TITRATIONS IN ALKALINE MEDIUM

I. TITRATION OF FERRICYANIDE

by

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Mercurous salts have a small reducing property but in the presence of a large concentration of thiocyanate ions these reducing properties are enhanced as a consequence of the formation of the $[Hg(SCN)_4]^{-2}$ complex. This enhancement has been applied in quantitative analysis by BRADBURY AND EDWARDS[1] to the direct titration of ferric salt. Later, PUGH[2], and BELCHER AND WEST[3] have carried out a study of these titrations. Some other applications have been studied by these authors[4] and the present[5].

In spite of the great interest these reagents have acquired, there are no references concerning titrations in alkaline medium with mercurous salts as reagents.

In alkaline medium, mercurous salts yield HgO and Hg. But in the presence of complex-forming ions with Hg^{+2}, the HgO precipitate is not produced but instead the respective complex is formed. For instance, in the presence of SCN^-, CN^- or I^-, we have noticed that many oxidizing substances are reduced in alkaline medium, and $[Hg(SCN)_4]^{-2}$, $[Hg(CN)_4]^{-2}$ and $[HgI_4]^{-2}$, respectively, are formed.

The most important redox titration in alkaline medium is that of ferricyanide, not only on account of its own interest, but also because it is able to conduce to a great number of indirect titrations. In fact, potassium ferricyanide has been used for the titrations of arsenic, antimony, vanadium salts, sulphur compounds, hydrogen peroxide, sugars, hydrazin sulphate and other organic compounds.

In spite of this, the number of direct titrations for ferricyanide is rather small: DEL FRESNO AND VALDÉS[6] used vanadyl sulphate for this titration in strong alkaline solution and in the absence of air. HAHN[7] used chromic salt in concentrated NaOH. DICKENS AND MAASSEN[8] reduce with cobaltous salt in an ammonia-ammonium chloride buffer. WILLIARD AND MANALO[9] used hydrogen peroxide in a hot basic medium.

No reference has been found to titration with mercurous salt in the presence of enhancing substances.

In the presence of cyanide the titration is not convenient since the cyanide anion is oxidised by the ferricyanide. In the presence of thiocyanate the titration

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is not convenient either, since a precipitate (mercuric oxide, mercurous and mercuric ferro- and ferricyanide) totally insoluble in an excess of thiocyanate is formed.

When iodide is present the results obtained are satisfactory. The ferricyanide is reduced quantitatively to ferrocyanide, the mercurous salt being oxidised to soluble $[HgI_4]^{-2}$, and the end-point can be detected potentiometrically (the change of potential at the end-point being about 150 mv), or with diphenylamine sulphonate.

In a strong alkaline medium the ferricyanide has no effect on iodide (Fig. 1).

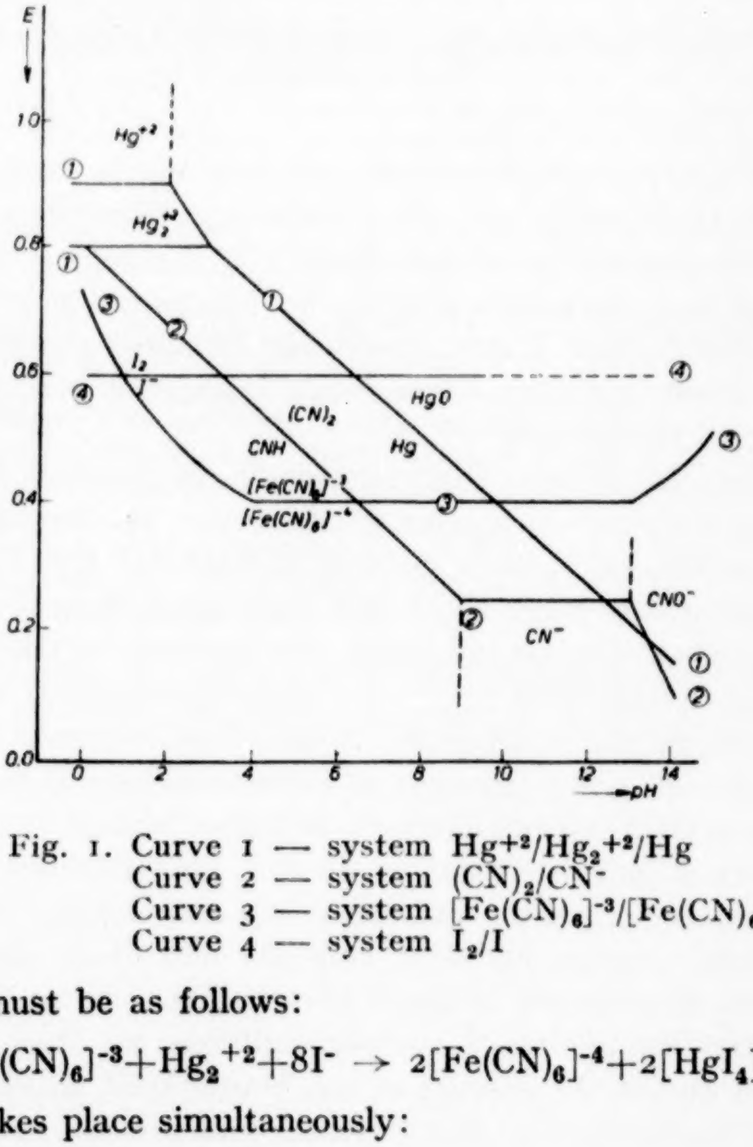

Fig. 1. Curve 1 — system $Hg^{+2}/Hg_2^{+2}/Hg$
Curve 2 — system $(CN)_2/CN^-$
Curve 3 — system $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$
Curve 4 — system I_2/I

The reaction must be as follows:

$$2[Fe(CN)_6]^{-3} + Hg_2^{+2} + 8I^- \rightarrow 2[Fe(CN)_6]^{-4} + 2[HgI_4]^{-2}$$

but this other takes place simultaneously:

$$Hg_2^{+2} + 4I^- \rightarrow [HgI_4]^{-2} + Hg$$

$$Hg + 2[Fe(CN)_6]^{-3} + 4I^- \rightarrow 2[Fe(CN)_6]^{-4} + [HgI_4]^{-2}$$

In both ways the total reaction is the same and it is only necessary to have a concentration of iodide high enough, at least 0.2*M*, to help the formation of intermediate compounds (mercuric iodide and ferrocyanide).

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The results obtained are correct, the usual volumetric errors being obtained.

The titration must be carried out at temperature below 30° C. Otherwise, high results can be obtained since the iodide and the ferricyanide react.

The acidity of the reagent must be controlled, since with solutions containing much free mineral acidity wrong results are obtained. In this way, a solution of mercurous perchlorate prepared as described must be preferred to that of mercurous nitrate, since the hydrolytic effect is less, it can be kept at a higher value of pH.

The influence of the different anions has been considered. Anions having oxido-reducing properties in alkaline medium do interfere. Chloride, nitrate and sulphate do not interfere in fairly high concentration.

The great advantage of the method over those previously proposed is the non-interference of the air on the reagent and during the titration.

EXPERIMENTAL PART

Reagents

Mercurous perchlorate must be preferred to the nitrate since the solution is more stable and can be obtained less acid without hydrolytic precipitation. This compound is obtained from the following substances:

Red mercuric oxide, 26 g
Perchloric acid ($d = 1.5$), 30 ml
Metallic mercury, 30 g
Water, 50 ml

These substances are mixed thoroughly, stirring and heating till soluiton of mercuric oxide. The solution is filtered, and diluted to 2000 ml. It is titrated as mercurous chloride.

Potassium ferricyanide 0.1*N*. By solution of pure Merck salt. It is titrated by iodometry periodically.

Potassium iodide, 1M

Sodium hydroxide, 4M.

Influence of pH

Procedure. 10 ml of ferricyanide solution in a volume of 100 ml containing 40 ml of iodide solution are titrated with mercurous perchlorate. The pH is measured with the glass electrode. The usual potentiometric technique with platinum wire and calomel saturated electrode is followed. The results are included in Table I.

During the titration it is noticed that at the moment the mercurous salt drop falls on the solution a dark-black precipitate is formed, which is quickly dissolved, and the yellow colour of the ferricyanide decreases. At the end-point the reaction is rather slow and it is advisable to proceed slowly.

TABLE I

Solutions. 1. potassium ferricyanide, 0.1*N* (f = 0.982)
2. mercurous perchlorate, 0.1*N* (f = 1.014)
In all cases 10 ml of ferricyanide solution, or 9.82 ml of ferricyanide solution 0.1000*N* are titrated.

Conditions of pH	ml of $Hg_2(ClO_4)_2$ consumed	ml of $K_3[Fe(CN)_6]$ 0.1*N* found	Difference %
Saturated solution of $NaHCO_3$; pH = 8.5	10.48	10.64	+ 8.5
Buffer solution NH_4Cl-NH_3; pH = 9.0	10.10	10.24	+4.3
1% solution of Na_2CO_3; pH = 10.8	10.58	10.73	+9.2
1*M* NH_3 solution pH = 11.5	9.95	10.09	+2.7
0.1*M* NaOH solution pH = 12.7	10.20	10.34	+5.2
0.5*M* NaOH solution pH = 13.2	9.90	10.05	+2.3
0.65*M* NaOH solution pH = 13.6	9.85	9.99	+1.7
1*M* NaOH solution pH = 14	9.70	9.84	+0.2
2*M* NaOH solution pH = > 14	9.70	9.84	+0.2
2.6*M* NaOH solution pH = > 14	9.68	9.82	0.0
3*M* NaOH solution pH = > 14	9.65	9.79	—0.3
4*M* NaOH solution pH = > 14	9.75	9.89	+0.6

Observations. For a pH less than 14 the values obtained are high. In the presence of a 1-5*M* NaOH solution the results are correct.

Influence of the concentration of iodide

The experiments are carried out in 1*M* NaOH solution. The same conditions before described are used, but the iodide concentration is variable. The results are included in Table II.

TABLE II

Solutions. 1. potassium ferricyanide 0.1N (f = 0.974)
2. mercurous perchlorate 0.1N (f = 1.014)

In all cases 10 ml of solution equivalents to 9.74 ml 0.1000N ferricyanide solution are titrated.

Concentration of KI solution	ml of $Hg_2(ClO_4)_2$ consumed	ml of $K_4[Fe(CN)_6]$ 0.1000N found	Difference %
0.1M	10.33	10.48	+7.5
0.15M	10.30	10.45	+7.3
0.2M	9.75	9.89	+1.5
0.25M	9.65	9.79	+0.5
0.3M	9.65	9.79	+0.5
0.4M	9.60	9.73	—0.1
0.5M	9.63	9.76	+0.2

Observations. The solution must be at least 0.2M in KI; high results being obtained for smaller concentrations. If the iodide concentration is less than 0.1M a yellow precipitate is formed, insoluble in this iodide concentration.

Influence of the concentration of ferricyanide

The concentration of ferricyanide is variable; the concentration of iodide and NaOH being 0.4M and 1M, respectively. The results are included in Table III.

TABLE III

Solutions. 0.1N potassium ferricyanide (f = 0.975)
0.1N mercurous perchlorate (f = 1.020)

ml 0.1000N (correct) of ferricyanide added	ml of 0.102N $Hg_2(ClO_4)_2$ consumed	ml of 0.1000N ferricyanide found	Difference %
4.88	4.80	4.90	+0.4
9.75	9.55	9.74	—0.1
14.63	14.30	14.59	—0.2
19.50	19.10	19.48	—0.1
24.38	23.90	24.38	0.0
29.25	28.70	29.27	+0.1

Observations. It can be observed that the results are all correct for the iodide concentration proposed and the usual ferricyanide amount.

Influence of the time

10 ml of 0.0982*N* potassium ferricyanide were titrated with mercurous perchlorate. In every case the time was measured from the moment at which the ferricyanide and the iodide were brought together till the moment at which the titration was commenced. The results are as follows (Table IV).

TABLE IV

Solutions. 0.1*N* potassium ferricyanide (f = 0.982)
0.1*N* mercurous perchlorate (f = 0.952)

In all cases 10 ml of solution equivalents to 9.82 ml 0.1000*N* correct ferricyanide solution are titrated.

Time (minutes)	ml of $Hg_2(ClO_4)_2$ 0.0952*N* consumed	ml of $K_3[Fe(CN)_6]$ 0.1000*N* found	Reduced ferricyanide in %
1	10.30	9.81	0.1
2	10.30	9.81	0.1
3	10.30	9.81	0.1
4	10.25	9.76	0.5
4.5	9.95	9.48	3
5	9.65	9.19	7
10	9.30	8.85	9.9
20	8.80	8.38	15
60	6.48	6.17	27
24 hours	1.00	0.95	91

Observations. The reaction between the ferricyanide and the iodide is very slow, but it seems that once it is initiated it continues more rapidly. From the practical point of view, it is evident that it is convenient to add the iodide just at the moment the titration is to be commenced.

Influence of the temperature

The different solutions are heated before they are mixed. During the titration with the cold mercurous salt the temperature decreased. The initial and final temperatures are shown in table V.

TABLE V

Solutions. 0.1*N* potassium ferricyanide (f = 0.982)
0.1*N* mercurous perchlorate (f = 0.952)

In all cases 10 ml of solution equivalents to 9.82 ml 0.1000*N* (correct) ferricyanide solution are titrated.

Initial temperature	Final temperature	ml of $Hg_2(ClO_4)_2$ 0.0952*N* consumed	ml of $K_3[Fe(CN)_6]$ 0.1000*N* found	Reduced ferricy. %
10° C	12° C	10.30	9.81	0.1
20	20	10.32	9.82	0.0
25	22	10.28	9.79	0.3
30	28	10.25	9.76	0.6
40	35	10.10	9.62	2
70	62	9.80	9.33	5

Observations. The results are only correct for a temperature below 30° C. Above this temperature a reaction between the iodide and the ferricyanide cannot be excluded.

Influence of the acidity of the reagent

All the experiments described above have been made with a reagent containing very small amounts of free acid. In the following tables experiments made with different mercurous perchlorate and nitrate solutions show that when the pH the solution decreases the results increase. In general, a reagent of very slight acidity must be used.

The results are included in Table VI.

TABLE VI

Solutions. 0.1 *N* potassium ferricyanide (f = 0.975)
0.1 *N* mercurous perchlorate of varying acidity
0.1 *N* mercurous nitrate of varying acidity.

In all cases 10 ml of potassium ferricyanide solution equivalents to 9.75 ml 0.1000*N* (correct) are titrated.

pH of $Hg_2(ClO_4)_2$ solution	ml of $K_3[Fe(CN)_6]$ 0.1000*N* found	Difference %
3.0	9.74	—0.1
3.0	9.79	+0.4
3.0	9.77	+0.2
1.8	9.80	+0.5
1.8	9.80	+0.5
1.8	9.78	+0.3
1.0	10.02	+2.7
1.0	9.98	+2
1.0	10.08	+3
0.3	10.14	+4
0.3	0.96	+2
0.3	10.14	+4
pH of $Hg_2(NO_3)_2$ solution		
1.7	9.75	0.0
1.7	9.73	—0.2
1.7	9.70	—0.5
1.1	10.12	+3.8
1.1	9.98	+2.3
1.1	10.03	+2.8
0.5	10.17	+4.3
0.5	9.96	+2
0.5	10.07	+3

Influence of the different anions

The influence of fairly large amounts of different anions has been tested. Nitrate, chloride and sulphate do not interfere at a concentration of 5%. Some oxidizing anions such as IO^-, BrO^- and ClO^- do interfere through their oxidizing power. The reducing agents S^{-2}, SO_3^{-2}, $S_2O_3^{-2}$, AsO_2^{-2} and CN^- interfere.

Titration with internal reversible indicator

All the above experiences were carried out with potentiometric indication of the end-point. Looking for a chemical indicator, methylene blue, picric acid and ferrous dimethylglyoxime were tried, but the results were poor, a sharp end-point not being obtained.

Recently, WILLARD AND MANALO[9] have proposed the use of some derivatives of diphenylamine; barium diphenylamine sulphonate seems to be the most suitable. In fact, the green form of this indicator obtained according to WILLARD AND YOUNG[10] have proved quite suitable. At the end-point a change from red to colourless is obtained. Table VII shows some titrations with this indicator.

TABLE VII

Solutions. 0.1*N* potassium ferricyanide (f = 0.975)
0.1*N* mercurous perchlorate (f = 1.020)

ml of 0.1000*N* (correct) ferricyanide added	ml of 0.1000*N* ferricyanide found: Potentiometrically	ml of 0.1000*N* ferricyanide found: With indicator	Difference % (with indicator)
4.88	4.85	4.90	+0.4
9.75	9.74	9.78	+0.3
14.63	14.58	14.70	+0.5
19.50	19.48	19.53	+0.2
24.38	24.38	24.48	+0.4
29.25	29.30	29.30	+0.2

PROCEDURE PROPOSED

Taking into account the whole study and the considerations indicated in the last paragraph, the following procedure has been proposed for the titration of ferricyanide with mercurous salt:

To cold solution containing the ferricyanide are added 25 ml of 4*M* NaOH, the necessary amount of water to give a final volume of 100 ml; and 40 ml of 1*M* potassium iodide just as the titration is going to be started. Four drops of the indicator diphenylamine sulphonate alkaline oxidized form are added (or the electrode introduced if the potentiometric method is followed) and the standard solution of the mercurous perchlorate is immediately added. Near the end-point this addition is made slowly. With potentiometric determination a sharp 100 mv change can be observed, and with the indicator the characteristic change from red to colourless.

SUMMARY

For the first time the application of mercurous salt for reductimetric titrations in alkaline medium has been studied. In the presence of iodide the ferricyanide ion can be titrated accurately. The end-point can be determined potentiometrically or with barium diphenylamine sulphonate. The influence of the concentration of iodide, ferricyanide and alkali, temperature, acidity of the reagent, and time are considered. The greater advantage of this procedure lies in the fact that the reagent is stable to air and the titrations can be carried out without elimination of the latter.

RÉSUMÉ

Pour la première fois, l'utilisation des sels mercureux pour les titrations réductimétriques, en milieu alcalin, a été envisagée. En présence d'iodure, l'ion ferricyanhydrique peut être titré avec précision. Le point final est déterminé par potentiométrie ou au moyen de diphénylaminesulfonate de baryum. L'influence de la concentration en iodure, ferricyanure et hydroxyde alcalin, de la température, de l'acidité du réactif et du temps, est étudiée. Le plus grand avantage de cette méthode est que le réactif est stable à l'air; les titrations peuvent donc être effectuées sans chasser celui-ci.

ZUSAMMENFASSUNG

Zum ersten Mal wurde die Anwendung eines Hg^+-salzes bei der reduktimetrischen Titration im alkalischen Medium untersucht. Bei der Gegenwart von Jodid kann das Ferricyanation genau titriert werden. Der Endpunkt kann potentiometrisch oder mit Bariumdiphenylamindisulfonat bestimmt werden. Der Einfluss der Konzentration von Jodid, Ferricyanid und Alkali, der Temperatur, des Säuregrades der Reagenzien und der Zeit werden erwogen. Der grössere Vorteil dieses Verfahrens liegt in der Tatsache, dass das Reagenz an der Luft beständig ist und die Titration so ohne Ausschluss der letzteren durchgeführt werden kann.

SUMARIO

Ha sido estudiada por primera vez la aplicación de las sales mercuriosas en las valoraciones reductimétricas en medio alcalino. En presencia de ioduro el ión ferricianuro puede ser valorado exactamente. El punto final puede ser determinado potenciométricamente o con difenilaminsulfonato bárico. Se estudian la influencia de la concentración de ioduro, ferricianuro y álcali, de la temperatura, acidez de la reacción y del tiempo. La mayor ventaja de este procedimiento se halla en el hecho de que el reactivo es estable al aire y la valoración puede ser llevada directamente sin previa eliminación del mismo.

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ON THE VOLUMETRIC DETERMINATION OF HYDROGEN SULFIDE AND SOLUBLE SULFIDES

by

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Methods using potassium iodate as the oxidizing agent

In an earlier communication[1] in this series, methods for the determination of sulfides, using sodium hypochlorite or potassium permanganate as the oxidizing agent were discussed. In these procedures the sodium sulfide, contained in strong alkali, was oxidized by an excess of oxidant. After oxidation, this excess was determined by adding potassium iodide and acidifying. The iodine liberated was back-titrated with sodium thiosulfate. It was found that the yield never reached the theoretical, either because the oxidation was not complete or because the oxidant was destroyed, which made it difficult to draw reliable conclusions from the results. It seemed therefore interesting to try other oxidants, which are more likely to be stable in strongly alkaline solutions.

Potassium iodate is known to be a very stable reagent and was therefore tried. First the stability of potassium iodate in strong alkaline solution was studied. A potassium iodate solution was prepared and was standardized against sodium thiosulfate after addition of potassium iodide and sulfuric acid. Fifteen ml of the iodate solution consumed 17.71 ml of $0.1N$ sodium thiosulfate solution. Then the same amount of potassium iodate was boiled with various amounts of $10N$ sodium hydroxide. Even refluxing for half an hour with 10 ml of the sodium hydroxide solution did not change the consumption of thiosulfate, thus showing that potassium iodate is perfectly stable in a boiling $4N$ sodium hydroxide solution. This is not the case for sodium hypochlorite nor potassium permanganate[1], and thus potassium iodate in this respect is the best oxidant of the three.

The oxidation was studied employing the same technique as before[1]. A sodium sulfide solution was prepared according to KIRSTEN AND CARSTENS[2] and standardized. It was found to contain 0.244 ± 0.0012 milligrams of sulfur per ml (mean of six values). Ten ml portions of this solution were mixed with 14.98 ml of a $0.1160N$ potassium iodate solution and 10 ml $10N$ sodium hydroxide solution and boiled gently for ten minutes. After cooling 5 ml of a five per cent. potassium iodide solution and 20 ml of a $8N$ sulfuric acid were added. The liberated iodine was estimated by titration with $0.0995N$ thiosulfate solution.

The following values were obtained:

Ml thiosulfate consumed:	11.38	11.41	11.42	11.33	11.30	11.29
Milligrams sulfur found:	2.42	2.41	2.40	2.44	2.46	2.46

The mean value is 2.43 ± 0.025 milligrams of sulfur in 10 ml of the sulfide solution. This value indicates that after ten minutes boiling at a hydroxide concentration of $4N$ the oxidation is quantitative within experimental errors. Further experiments showed that the oxidation in most cases was complete after only a few minutes boiling, but that oxidation at room temperature gave a yield of only 95 per cent. When the sodium hydroxide concentration was lowered to $3.5N$, the yield was still 100 per cent., but at $1.0N$ the yield was of the order of 98 per cent. Apparently the optimum conditions are obtained if the procedure given above is followed.

It may be concluded, that oxidation of sulfides to the sulfate state by potassium iodate under the conditions given, is quantitative within experimental error and forms a better basis for the estimation of sulfides than do methods employing the oxidants sodium hypochlorite and potassium permanganate, mainly dependent on the fact that these reagents are decomposed by boiling with strong alkali, and potassium iodate is not. It is apparently true that quantitative oxidation to the sulfate state is rather difficult if the solution is not hot or very strongly alkaline. However, if these conditions are maintained, the question is not to find a strong oxidant, but to find an oxidant that is stable in these solutions. Potassium iodate is such an oxidant.

Kirsten[3], who has continued this work, reports that highly accurate and sensitive, direct and indirect methods for the colorimetric ultramicrodetermination of sulfide can be based upon the iodate-oxidation procedure.

SUMMARY

The volumetric determination of sulfides using potassium iodate as the oxidizing agent is briefly investigated. A method is given which makes it possible to oxidize sulfides quantitatively to the sulfate state, and it is shown that it is superior to methods employing potassium permanganate and sodium hypochlorite.

RÉSUMÉ

Le dosage volumétrique des sulfures, utilisant l'iodate de potassium comme oxydant est brièvement examiné. Une méthode est proposée permettant d'oxyder les sulfures quantitativement à l'état de sulfates. Elle est plus avantageuse que les méthodes employant le permanganate de potassium et l'hypochlorite de sodium.

ZUSAMMENFASSUNG

Die volumetrische Bestimmung von Sulfiden unter Verwendung von Kaliumjodat als Oxydationsmittel wurde kurz untersucht. Es wird eine Methode gegeben, mit deren Hilfe es möglich ist Sulfide quantitativ zu Sulfaten zu oxydieren und es wurde gezeigt, dass diese Methode den Kaliumpermanganat und Natriumhypochlorit verwendenden Methoden überlegen ist.

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THE APPLICATION OF THIOSALTS IN ANALYSIS
II. ESTIMATIONS BASED ON DECOMPOSITION OF THIOSALTS
Part C. ESTIMATION OF GOLD, PLATINUM AND ANTIMONY

by

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In the earlier publications[1,2] of this series, the authors dealt with the quantitative estimation of arsenic, tellurium, selenium, molybdenum and tin. The method was based upon the decomposition of thiosalts of these metals by adding an excess of hydrochloric acid and weighing the sulphides thus obtained. It has been found possible to extend the method to gold, platinum and antimony also.

ESTIMATION OF GOLD

The well known method for the gravimetric determination of gold depends upon the reduction of the solution by reducing agents like sulphur dioxide, ferrous sulphate, hydrogen peroxide or oxalic acid, and weighing the precipitated metal. The reduction method takes from six to twelve hours, depending upon the reducing agent used, while the method depending upon the decomposition of thiosalt and weighing the precipitated sulphide takes only 2-3 hours and gives results which are comparable in accuracy with those obtained by the reduction method.

The solution was prepared by dissolving pure auric chloride (B.D.H.) in water and standardizing it by precipitating the metal either with sulphur dioxide[3] in an acid medium or with hydrogen peroxide[4] in an alkaline medium. Measured volumes of the solution were treated with an excess of 2*N* sodium sulphide reagent[5], about 20 ml of the alkali sulphide being required for every 50 mg of gold present in solution. In a neutral or alkaline solution, gold is directly converted into its thiosalt while in acid medium gold sulphide is first precipitated and then dissolves in an excess of the reagent. The solution containing the thiosalt is treated with an excess of 2*N* hydrochloric acid and heated to boiling. The precipitated sulphide is allowed to settle, filtered through a sintered glass crucible (porosity 4), washed with hot water, carbon disulphide, alcohol and ether successively, dried in a desiccator for about half an hour and weighed. Alternatively, the precipitated sulphide can be washed with hot water alone and dried in an air oven at 105-110° C for an hour and weighed as Au_2S_3. The results obtained are given in Tables I and II.

TABLE I

WASHING WITH ALCOHOL AND ETHER

Vol. of Au solution, in ml	Vol. of 2*N* Na_2S added in ml	Vol. of 2*N* HCl added in ml	Wt. of ppt. Au_2S_3 in g	Amt. of Au in the ppt. in g	Amt. of Au actually present in g
20	15	40	0.0584	0.0470	0.0470
	15	45	0.0585	0.0471	
	20	50	0.0585	0.0471	
25	15	45	0.0731	0.05884	0.05875
	20	50	0.0730	0.05876	
	20	50	0.0730	0.05876	
20	15	40	0.0237	0.01906	0.01900
	20	50	0.0236	0.01898	
	15	45	0.0236	0.01898	

TABLE II

WASHING WITH HOT WATER ALONE AND DRYING AT 100-110° C

Vol. of Au solution in ml	Vol. of 2*N* Na_2S added in ml	Vol. of 2*N* HCl added in ml	Wt. of ppt. Au_2S_3 in g	Amt. of Au in the ppt. in g	Amt. of Au actually present in g
25	15	50	0.0732	0.05892	0.05875
	20	50	0.0730	0.05876	
	20	45	0.0731	0.05884	
9	10	20	0.0263	0.02117	0.02115
	15	30	0.0263	0.02117	
	10	25	0.0262	0.02110	
25	15	50	0.0296	0.02380	0.02375
	15	40	0.0296	0.02380	
	20	50	0.0296	0.02380	

ESTIMATION OF PLATINUM

Platinum is generally estimated by precipitating it either as ammonium chloroplatinate[6] or as metal with formic acid[7]. The first method, which involves ignition of the chloroplatinate to metal, is very difficult and tedious. The second method is comparatively easy, but the complete reduction to metal takes about 24 hours. In the method based on the decomposition of the thiosalts, the platinum is precipitated as sulphide and then ignited to metal. The whole estimation can be completed within three hours.

The solution was prepared by dissolving pure platinic chloride (B.D.H.) in water and standardizing it by reduction with formic acid. Measured volumes of the solution were treated with an excess of $2N$ sodium sulphide reagent, about 25 ml of the alkali sulphide being required for every 50 mg of the metal present in the solution. The thiosalt which is immediately formed, giving a beautiful light red colour, is treated with an excess of concentrated hydrochloric acid and boiled for a minute for complete precipitation. The concentration of HCl in the resulting mixture should be at least $6N$, otherwise some platinum is likely to escape precipitation. The precipitate of platinum sulphide is allowed to settle, filtered through a gravimetric filter paper (Whatman 42) and washed with hot water first by decantation and then on filter paper. When the precipitate is completely free from chloride ions, it is ignited with the filter paper in a silica crucible over a Meker burner for about half an hour and weighed as metal. The results obtained in some of the experiments are given in Table III.

TABLE III

Vol. of Pt solution in ml	Vol. of $2N$ Na_2S added in ml	Vol. of $12N$ HCl added in ml	Wt. of ignited ppt *i.e.* Pt in g	Amt. of Pt actually present in g
25	30	60	0.0606	0.06070
	25	55	0.0605	
	25	50	0.0608	
20	20	50	0.0485	0.04856
	25	55	0.0486	
	25	50	0.0486	
25	15	50	0.0208	0.02080
	20	50	0.0208	
	20	45	0.0209	

ESTIMATION OF ANTIMONY

As the gravimetric method depending upon the precipitation of antimonious sulphide from an acid solution is very tedious, antimony is generally determined by volumetric methods[8]. But if the sulphide is precipitated by decomposing the

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thiosalt, the gravimetric estimation of antimony becomes very easy and provides a convenient alternative to the volumetric processes.

The solution of antimony was prepared by dissolving pure potassium antimony tartrate (A.R., B.D.H.) in water and standardizing it by titrating with iodine. Measured volumes of the solution were treated with an excess of 2*N* sodium sulphide reagent, about 20 ml of the alkali sulphide reagent being required for every 50 mg of the metal present in the solution. The thiosalt which is immediately formed, is decomposed by adding a slight excess of 2*N* hydrochloric acid and just boiling the mixture. The precipitate is allowed to settle, filtered through a sintered glass crucible (porosity 4), washed with hot water until it is completely free from chloride ions. It is then dried in an air oven at 105-110° C for an hour and weighed as Sb_2S_3. The following results were obtained.

TABLE IV

Vol of Sb solution in ml	Vol. of 2*N* Na_2S added in ml	Vol. of 2*N* HCl added in ml	Wt. of ppt Sb_2S_3 in g	Amt. of Sb in the ppt in g	Amt. of Sb actually present in g
25	20	40	0.0788	0.05646	0.05632
	15	40	0.0787	0.05640	
	15	35	0.0787	0.05640	
20	15	30	0.0630	0.04515	0.04506
	20	35	0.0631	0.04523	
	20	30	0.0630	0.04515	
28	20	30	0.0883	0.06330	0.06308
	30	60	0.0882	0.06323	
	20	60	0.0881	0.06316	

SUMMARY

The general method of forming and then decomposing the thiosalts has been applied to the gravimetric estimation of gold, platinum and antimony. In the case of gold and antimony the metals are weighed as Au_2S_3 and Sb_2S_3, respectively, while in the case of platinum, the precipitate of platinum sulphide is ignited and weighed as metal.

RÉSUMÉ

La méthode générale de formation et de décomposition des thiosels a été apppliquée au dosage gravimétrique de l'or, du platine et de l'antimoine. L'or et l'antimoine sont pesés à l'état de Au_2S_3 et Sb_2S_3 tandis que dans le cas du platine, le précipité de sulfure de platine est grillé; on pèse alors le platine formé.

ZUSAMMENFASSUNG

Die allgemeine Methode der Bildung und späteren Zersetzung der Schwefelwasserstoffsalze wurde zur gravimetrischen Bestimmung von Gold, Platin und

Antimon angewandt. Im Falle des Golds und des Antimons werden die Metalle als Au_2S_3 bzw. Sb_2S_3 gewogen und im Falle des Platins wird der Platinsulfidniederschlag geglüht und als Metall gewogen.

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AN APPARATUS FOR THE WET ASHING OF ORGANIC MATTER

by

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During the past year some research work has been done in this laboratory on methods for the determination of sulfur in wood, treated by the sulfite process. The sulfur content of the samples was rather low, of the order of one per cent., and dry combustion methods proved to be inapplicable. Wet ashing methods, where the substance was digested with mixtures of perchloric and nitric acids, were found to be satisfactory. Wet ashing procedures of this type have become more popular in the past few years and recently have been investigated thoroughly by SMITH[1]. In our first experiments, which were carried out in Kjeldahl flasks and flasks with reflux condensers of various types, only about 75 per cent. of the sulfur was retained. The investigation was then continued using pure, well defined sulfur-containing organic substances. For these experiments, the results of which will be presented later, an apparatus was constructed, which has proved to be so valuable for all types of investigations on ashing that it was considered justified publishing its construction separately.

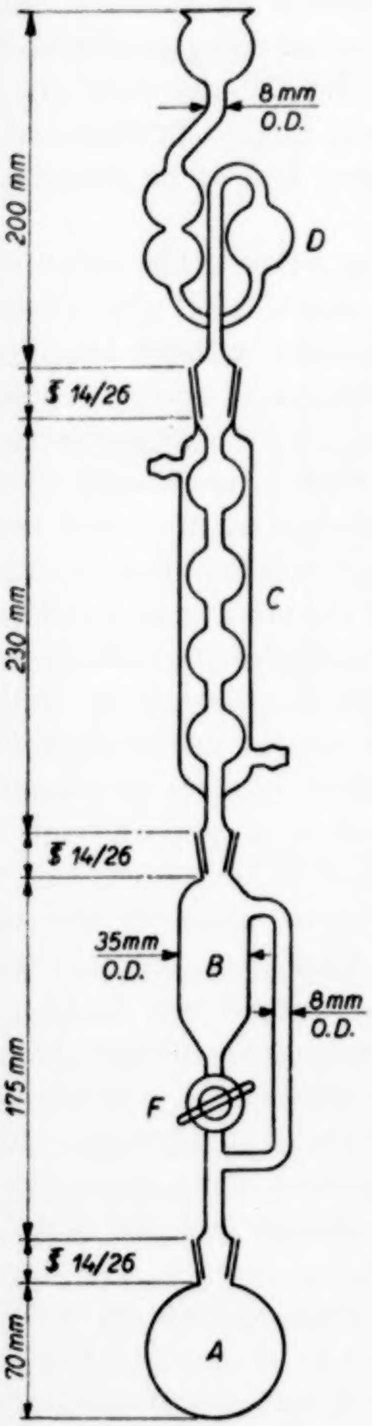

Fig. 1. Semi-micro apparatus wet combustion.

A semi-micro apparatus was first constructed of Pyrex glass using standard taper joints. Later a macro-apparatus of the same general design was built. The construction and the dimensions of the semimicro apparatus are shown in Fig. 1. It consists of four parts, a digestion flask A, a reflux collector, B, a reflux condenser C, and a top part D. The digestion flask is drawn as an ordinary round-bottomed flask, but it may be changed at will to a flat-bottomed flask,

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G. FREDERICK SMITH, *Anal. Chim. Acta*, 8 (1953) 397.

which is convenient if heating on a hot plate is desired. A two necked flask may be used if reagents are to be added during the digestion, the second neck being fitted with a dropping funnel. The reflux collector is provided with an oblique bored stopcock, F. When this stopcock is open the apparatus functions as a reflux condenser but if it is closed, the reflux from the condenser is collected and may be analysed separately, or after completing the ashing it may be added through the stopcock to the contents in the digestion flask. The reflux condenser is an ordinary Allihn condenser, and the top part makes it possible to wash the escaping gases with the desired reagent and to judge if gases are evolved during the reaction. (In an earlier model of the apparatus the escaping fumes were washed in washbottles of the ordinary type, and a carrier-gas, such as nitrogen, had to be introduced in the digestion flask to prevent sucking back.)

A method of combustion often applied is performed as follows. The substance, up to 1 gram, is weighed into the digestion flask. The top part is filled with washing liquid to such a level that gas may pass in both directions without the liquid splashing over. The acid mixture, *e.g.* 40 per cent. perchloric acid and 60 per cent. nitric acid, is poured directly into the digestion flask, or, if the substance reacts in the cold, into the reflux collector. The digestion flask is connected to the apparatus and the stopcock F is opened. The flask is heated until the nitric acid has reacted, that is, when the liquid in the top part indicates that no more gas is evolved. The stopcock is then closed and the rest of the nitric acid is collected in the reflux collector. During this operation the temperature of the acid mixture rises slowly, and when it reaches 150° C, the perchloric acid begins to oxidize the substance. This is indicated by white fumes, which appear in the flask. The heating is now regulated so that these fumes fill the reflux collector and dissolve in the nitric acid there, but they should not be allowed to ascend through the reflux condenser and the top part. This is done because it is suspected, but not yet proved, that these fumes mechanically carry away some of the constituents left in the acid mixture. When the substance has been digested some time with boiling perchloric acid, the temperature rises to about 200° C. In most cases the substance is completely oxidized when no more gases escape through the top part. In doubtful cases, a little chromic acid is added to the acid mixture. Complete oxidation is then indicated by the color of the acid turning orange, as described by SMITH[1]. When the digestion is completed, the apparatus is left to cool, and the liquids in the top part, reflux collector and the digestion flask are analyzed separately or together.

This method for wet ashing is given only as an example. It may be modified in numerous ways to fulfil special requirements. It must be understood that this apparatus is constructed for research work on analytical methods involving wet ashing, and, when a final method has been worked out, it may be modified in some ways.

When traces of elements are to be determined, it is often necessary to use up to five or ten grams of substance. For this reason the bigger macro apparatus was made, which has the same construction as the semimicro one, with the exception of a modified top part as shown in Fig. 2.

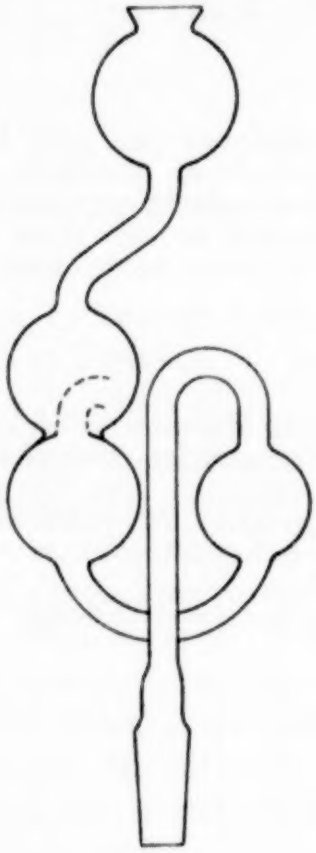

Fig. 2. Modified top part.

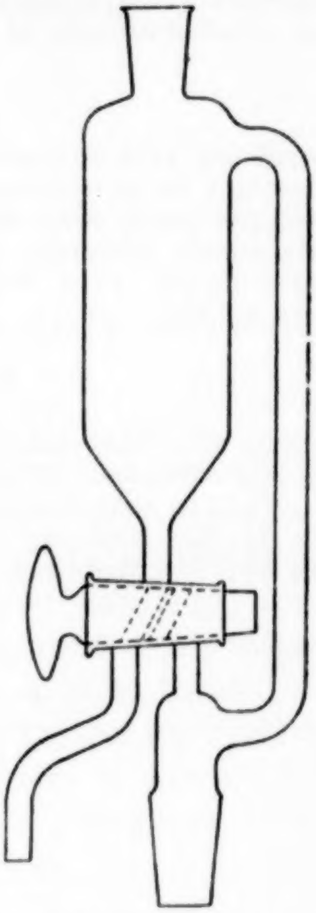

Fig. 3. Modified reflux collector.

In one apparatus the stopcock F was exchanged for a three-way stopcock as shown in Fig. 3. This makes it possible to empty the receiver when, for example, aqueous solutions are ashed. Both sets of apparatus are obtainable from the firm Werner-Glas, Slöjdgatan 1, Stockholm.

The main advantage of this apparatus lies in the possibility of analysing the escaping gases. After a wet ashing of some sulfur-containing substances, sulfate has been found in the top part as well as in the reflux collector and the digestion flask. The sum of these sulfate residues have been estimated and it was concluded that all the sulfur was quantitatively retained in the apparatus. This is true for all substances so far analyzed.

An other advantage is that it is not necessary to operate the apparatus in a hood. The semimicro type can be operated anywhere as it is, and if the macro apparatus is provided with a funnel, mounted upside down over the top part and connected to a water suction pump, all escaping gases can be removed safely.

SUMMARY

An apparatus for the wet ashing of organic material is described. It makes possible the ashing of large quantities of organic matter with pure, ash-free reagents and the determination of various constituents in the samples. This procedure is most useful for the determination of trace elements. It has mainly been used so far for the determination of small amounts of sulfur.

RÉSUMÉ

Un appareil de minéralisation de substances organiques par voie humide est décrit. Il permet la minéralisation de grandes quantités de matières organiques avec des réactifs purs, sans cendres, ne laissant pas de résidu par évaporation et le dosage de divers éléments de l'échantillon. Ce procédé est des plus utiles pour le dosage des traces. Il a été principalement utilisé pour déterminer de faibles quantités de soufre.

ZUSAMMENFASSUNG

Ein Apparat für Nassverbrennung von organischem Material wird beschrieben. Grosse Substanzmengen können mit aschefreien Reagenzien verbrannt werden und es ist möglich, verschiedene Bestandteile zu bestimmen. Der Apparat ist besonderes für die Bestimmung von Spurenelementen geeignet. Bis jetzt ist er hauptsächlich für die Bestimmung von kleinen Mengen Schwefel benützt worden.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES
LXII. DOSAGE DE L'YTTRIUM

par

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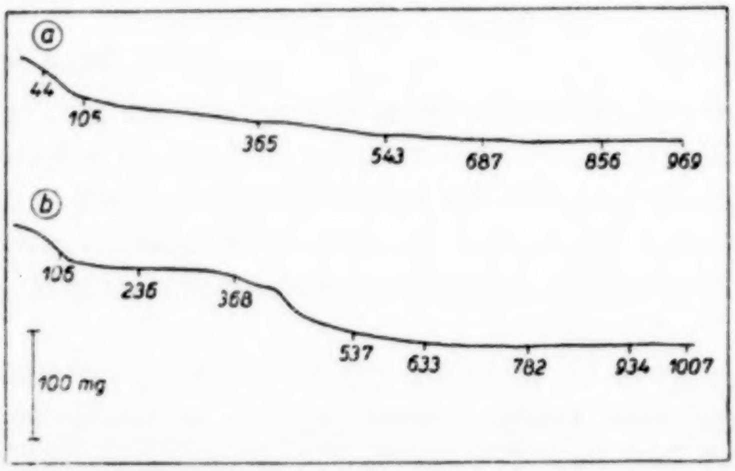
Les deux formes de pesée relatives à ce corps simple sont constituées par *l'hydroxyde* et *l'oxalate.*

Hydroxyde

Une solution de nitrate d'yttrium, sensiblement neutre, est traitée progressivement par l'ammoniaque diluée. Le précipité blanc gélatineux formé dépose pendant une nuit et on le filtre sur papier. La courbe de thermolyse réalisée en chauffage linéairement croissant à la vitesse de 300° par heure, sur un produit encore humide correspond à 81.45 mg d'oxyde Y_2O_3 (renfermant moins de 1/1000 d'oxyde d'holmium), est représentée sur la figure *a* et se montre décroissante jusqu'à 856° environ où commence le palier horizontal de l'oxyde Y_2O_3. Il n'existe aucune discontinuité permettant de manifester la formation de l'hydroxyde $Y(OH)_3$; par calcul sur la courbe originale, on trouve que ce dernier corps se formerait vers 365°.



Courbes de thermolyse des dérivés de l'yttrium *a*) Hydroxyde; *b*) Oxalate.

Oxalate

La solution de nitrate d'yttrium traitée par l'acide oxalique en milieu légèrement acide, au bain-marie, conduit à un précipité blanc très fin, vers 60°. On laisse déposer pendant une nuit et filtre sur papier. La courbe de thermolyse réalisée dans les mêmes conditions que ci-dessus, est représentée sur la figure *b* et montre que le point de départ, simplement séché à l'air, ne peut avoir la formule d'un hydrate à 9 H_2O. L'oxyde Y_2O_3 est complètement formé, pour la vitesse de chauffe indiquée, à 680°. Auparavant, il est impossible d'observer un palier horizontal correspondant à la formule de l'oxalate anhydre qui, par calcul, devrait apparaître vers 375°. Par contre entre 180 et 300°, on remarque un palier horizontal qui s'accorde approximativement avec la formule $Y_2(C_2O_4)_3.2H_2O$.

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* Pour LXI (Dosage du Palladium), voir *Anal. Chim. Acta*, 6 (1952) 250.

La seule forme de pesée de l'yttrium est donc l'oxyde Y_2O_3, lequel, comme toujours, apparaît à une température plus basse lorsqu'il dérive d'un oxalate plutôt que d'un hydroxyde.

J'ai l'agréable devoir de remercier M. le Prof. W. Klemm (Münster), Président de la Société chimique allemande, pour avoir bien voulu me faire parvenir l'échantillon relativement pur d'oxyde d'yttrium sans lequel ce travail n'eût pu s'effectuer.

RÉSUMÉ

On décrit les courbes de thermolyse de l'hydroxyde et de l'oxalate d'yttrium.

SUMMARY

The thermolysis curves of yttrium hydroxide and oxalate are described.

ZUSAMMENFASSUNG

Die Thermolysekurven des Yttriumhydroxyds und -oxalats werden beschrieben.

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SEPARATIONS OF PLATINUM METALS BY ION EXCHANGE
I. THE SEPARATION OF PALLADIUM FROM IRIDIUM*

by

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Only one application of ion-exchange resins to platinum metal chemistry is reported in the literature[4]. It deals with the concentration of platinum metals from waste residues. In the present paper, we report the separation of palladium from iridium using ion-exchange resins. The further use of ion-exchange resins in the separation of the four platinum group metals, palladium, platinum, rhodium and iridium from each other is being studied in this laboratory.

In approaching this problem it must be remembered that the platinum metals have tendencies to form complex chloride *anions* of the type $MeCl_x^{-y}$ and also complex ammine *cations* of the type $Me(NH_3)_x^y$. Both anion and cation behavior have been investigated and the fact that both occur may be an advantage even though it adds to the complexity.

APPARATUS AND REAGENTS

The ion-exchange columns used in this work were similar to those of TOMPKINS[6], but the sintered glass disk used to support the resin was replaced by the male part of a ground glass joint which was sealed off. The seal was perforated to allow passage of the eluate. A wad of glass wool was placed between the perforated base and the resin. The resin column was approximately 50 cm in length and 1 cm in diameter.

Following a preliminary survey of the behavior of a number of cation and anion resins toward platinum metals, certain resins were selected for further study. They were the cation resins Amberlite IR-100 and Dowex 50 and the anion resins Amberlite IR-4B, Dowex 1 and Dowex 2. They showed high capacity and yet metals could usually be eluted from them.

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* From a thesis submitted by WARREN B. CRUMMETT to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree Doctor of Philosophy.

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The resins were prepared for use by allowing the resin to stand overnight in a 2% solution of the ion which would convert the resin to the desired form. The wet resin slurry was then poured into the column previously filled with distilled water. The column was drained as necessary in order to add more slurry. Care was taken not to allow the level of liquid in the column to fall below the top of the resin. The resin column was then washed with distilled water until an approximately neutral eluate was obtained.

Reagent grade chlorides of Pd and Ir (American Platinum Works) were used as starting materials. Strong water solutions were prepared and evaporated first with nitric acid and then with hydrochloric acid. The residues were finally heated at 100° C to remove excess hydrogen chloride. This method gives solutions of reproducible behavior.

ANALYTICAL TESTS FOR PLATINUM METALS

Both qualitative and quantitative tests for small amounts of platinum metals are needed in order to follow the separations achieved by ion-exchange. The following qualitative tests were frequently used:

Palladium. Place one drop of acidic test solution on filter paper impregnated with nickel dimethylglyoxime. Dry the paper over a hot plate and then bathe it in 1*N* hydrochloric acid. The paper turns white except where palladium is present. Five-hundredths gamma of palladium is detectable[2].

Iridium. Evaporate the test solution to dryness. Add 4-5 ml of concentrated sulfuric acid and 2 ml of nitric acid and evaporate to fumes. A violet color indicates iridium. Although SANDELL[5] describes this test as insensitive, BEAMISH AND HILL[1] found it to be as sensitive as Pollard's test which uses perchloric acid and lithium sulfate and is sensitive to 0.5 gamma of iridium.

Solutions containing mixtures of these metals were evaporated to dryness and analyzed qualitatively by spectrographic means.

Quantitative estimations of amounts greater than 1 mg in mixtures of the metals were made by the GILCHRIST-WICHERS[3] scheme. The solution to be analyzed was freed from organic matter and volatile salts by evaporation to dryness, and ignition followed by treatment with hydrochloric and nitric acids and evaporation to dryness. The resulting residue was dissolved in a small amount of water and transferred to a porcelain crucible for the determination of palladium and iridium. Palladium was precipitated with dimethylglyoxime, filtered through a porcelain filter crucible, dried at 110° C and weighed. Iridium was precipitated as the hydrous oxide, filtered, and ignited in hydrogen to the metal.

A colorimetric method for estimating small amounts of iridium was also developed and will be described in detail in a separate publication. It is based on the formation of a violet color in nitric and sulfuric acids. Maximum extinction occurs at 575 mμ and the solution obeys Beer's law over the range 0.03 to 0.12 mg of iridium per milliliter.

EXPERIMENTAL

Tetrachloropalladous and hexachloroiridic anions are quantitatively adsorbed by the anion exchange resins Amberlite IR-4B, Dowex 1 and Dowex 2 but not at all by the cation resins Amberlite IR-100 and Dowex 50. This should make possible the quantitative separation of these two metals from other metals which do not form complex chloride anions. This point is being studied in a separate research.

Adsorption bands were visible on Dowex 1 and Dowex 2. Palladium, present as $PdCl_4^{-2}$, gave a dark red band; iridium, as $IrCl_6^{-2}$, gave a dark red band.

Attempts to elute the complex chloride anions from Dowex 1 and Dowex 2 were unsuccessful. Only slight elution occurred. Ammonium hydroxide brought about rapid elution, apparently, as a result of converting the chloride anions to ammine cations of the type $Me(NH_3)_x^y$. This elution was pronounced with palladium, less so with iridium. The addition of ammonium chloride also depressed the elution of iridium but did not decrease that of palladium. Thus a solution containing both 0.025*M* ammonium hydroxide and 0.025*M* ammonium chloride seems ideal for the separation of palladium and iridium which have been adsorbed as complex chloride anions on an anion resin. The separation is quantitative. Other bases thought to give complexes of the ammine type were also used as eluants. Aniline and piperidine showed a satisfactory elution behavior but had no advantage over ammonia.

Separation of palladium from iridium. Palladium as $PdCl_4^{-2}$ and iridium as $IrCl_6^{-2}$ are both quantitatively adsorbed by Dowex 1 and Dowex 2. Elution of Dowex 1 with an ammonium hydroxide-ammonium chloride mixture does not give a sharp separation of the two metals. With Dowex 2, palladium is quantitatively eluted in a spectrographically pure form using an eluant which is not more than 0.025*M* in both ammonium hydroxide and ammonium chloride. Iridium is not removable from these resins however with either strong acid or ammonium hydroxide.

The separation of palladium from iridium is better with Amberlite IR-100, a cation resin. This has the advantage that both metals can be recovered. The mixture of $PdCl_4^{-2}$ and $IrCl_6^{-2}$ ions is treated with ammonium hydroxide before it is added to the column. This converts the palladium to the cation ammine, $Pd(NH_3)_4^{+2}$, but has no apparent effect on the $IrCl_6^{-2}$ ion. The mixture is then passed through the cation resin Amberlite IR-100. Palladium is quantitatively retained while iridium passes quantitatively into the eluate. Palladium can then be removed quantitatively from the resin by elution with 1*M* hydrochloric acid.

Procedure for separation of palladium from iridium. The sample should contain not more than 10 mg of each of the metals. Evaporate the solution to dryness several times with hydrochloric acid. On the last evaporation, avoid heating the residue above 100° C. Dissolve the residue in 20 ml of distilled water and add 5 ml of concentrated ammonium hydroxide. Stir the mixture and pass it through an Amberlite column at a rate of 10 ml per minute. Wash the column with an ammonium hydroxide-ammonium chloride solution, 0.025*M* in each. Usually, iridium is completely removed after 50 ml of ammonium hydroxide-ammonium chloride eluate have been passed through the column. The color of the eluate may be used as a general guide to indicate the complete removal of iridium. The use of double the volume of wash solution over that required to the disappearance of color in the eluate provides a wide margin of safety.

Following separation of the iridium from the column, 50 ml of 1*M* hydrochloric acid is used as eluant to remove the palladium. This is followed by another 50 ml of water. Table I shows sample data on the separation of palladium from iridium.

TABLE I

SEPARATION OF PALLADIUM FROM IRIDIUM WITH AMBERLITE IR-100

Metal taken grams		Metal unadsorbed on column grams		Metal eluted with 1*M* HCl grams	
Pd	Ir	Pd	Ir	Pd	Ir
0.0118	0.0082	0.0000	0.0081	0.0118	0.0000
0.0118	0.0082	0.0000	0.0080	0.0117	0.0000
0.0118	0.0082	0.0000	0.0083	0.0119	0.0000

DISCUSSION

The separation of palladium and iridium is based upon the pronounced difference in their tendencies to be converted from complex chloride anions to complex ammine cations. Palladium ammine is apparently a much stronger complex than iridium ammine. There is in fact no evidence from the present work of any tendency for iridium to form the ammine. On the other hand the complex iridium chloride anion appears more stable than does that of palladium. There is obviously a competition between the anion and cation complexes for each metal and advantage is taken of this in the separation.

The separation achieved with the anion Dowex 2 has the disadvantage that iridium cannot be removed from the resin. It would be necessary to ignite the resin matrix in order to recover the iridium. This limitation is however absent when the cation resin Amberlite IR-100 is used. Iridium, as $IrCl_6^{-2}$ or $IrCl_6^{-3}$, even in strong ammoniacal solution passes through the resin quantitatively. Palladium as $Pd(NH_3)_4^{+2}$ is completely retained and is later removable by elution with 1*M* hydrochloric acid. The use of Amberlite IR-100 therefore is preferred.

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SUMMARY

Palladium and iridium are separated by passing an ammoniacal solution of the chlorides over Amberlite IR-100 resin. Palladium is retained as $Pd(NH_3)_4^{+2}$ while iridium, as $IrCl_6^{-3}$, passes through the column quantitatively. Palladium is then removed from the column by elution with 1*M* hydrochloric acid.

RÉSUMÉ

Le palladium et l'iridium sont séparés par passage d'une solution ammoniacale de leur chlorure sur la résine Amberlite IR-100. Le palladium est retenu sous forme de $Pd(NH_3)_4^{+2}$, tandis que l'iridium traverse la colonne quantitativement, sous forme de $IrCl_6^{-3}$. Le palladium est ensuite déplacé de la colonne par élution à l'acide chlorhydrique *M*.

ZUSAMMENFASSUNG

Palladium und Iridium werden getrennt indem man eine ammoniakhaltige Lösung des Chlorids über Amberlite IR-100 Harz führt. Palladium bleibt als $Pd(NH_3)_4^{+2}$ zurück während Iridium als $IrCl_6^{-3}$ durch die Chromatographieröhre mengenmässig geht. Palladium wird dann von der Chromatographieröhre enfernt durch Auswäsche mit 1*M* Chlorwasserstoff.

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THE RELATION BETWEEN CONCENTRATION AND TOTAL OPTICAL DENSITY IN RADIAL INORGANIC PAPER CHROMATOGRAPHY

by

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In the course of chromatographic research on filter paper, investigating the relation between the area of the spots produced by various amino acids and the concentration of the solutions used, FISCHER, PARSON AND MORRISON[1] have arrived at the conclusion that a linear relationship exists between the logarithm of the latter and the area of the former. BRIMLEY[2] provides the theoretical derivation of such a relation with the statement that equations analogous to those already developed for the theory of the flow of heat can be applied to the spot that expands by diffusion, brought on by the mobile phase.

VENTURELLO AND GHÉ[3] have confirmed, extending it to the inorganic field, that the relationship is valid for amino acids. Experimenting on cations, they adopt, with few modifications, RUTTER'S[4] radial technique, with which chromatograms are obtained that, when developed, have the appearance of rings or bands. The areas of the respective bands obtained by different concentrations are measured with a planimeter and the average values obtained, plotted against the logarithm of the concentration, give rise to a straight line. The existence of a linear relationship between the width of the band and the logarithm of the concentration, which has also been verified experimentally by VENTURELLO AND GHÉ and which could be deduced, knowing the proportionality between the area and the width of the circular crown, makes it possible to proceed from the measurement of the first to the knowledge of the second.

ZIMMERMANN AND NEHRING[5], using RUTTER'S radial technique with slight modifications, and experimenting on various amino acids at various concentrations, observe that the knowledge of the planimetric areas of the chromatograms is, in itself, insufficient to provide a quantitative answer; for this reason they consider it necessary to take into account also the intensity of the colours of the band, and, relying on the measurement of the optical density, they multiply the planimetric value by the densitometric one to obtain the concentration of the amino acids under examination.

From the above account it seems of interest to investigate the nature of the relation existing between the value of the total optical density of the bands and the corresponding concentrations of the ions that have caused it.

RUTTER's radial technique was chosen for this investigation, as modified by BERLINGOZZI AND SERCHI[6], who use, instead of the "tail", a paper pyramid whose top, as sharp as possible, is placed in contact with the centre of the disc, where the spot is applied, and whose base stands in the mobile phase.

Investigations have been carried out on the following cations:

$$Ag^+,\ Tl^+,\ Pb^{+2},\ Cu^{+2},\ Cd^{+2},\ Ni^{+2},\ Co^{+2},\ Ba^{+2},$$

all coming from their respective nitrates. Among the numerous complex-forming mixtures considered with a view to producing clearly outlined chromatograms, the most satisfactory result was given by the mixture proposed by POLLARD AND MCOMIE[7]: 0.5 g benzoylacetone, 50 ml butanol, 50 ml 0.1 N HNO_3. The temperature of the experiment was kept at about 20° C. The paper discs (Whatman No. 1) are developed when the distance from the point of application and the front of the mobile phase is 9.5 cm. The volume used for each experiment was 0.05 ml of solutions in various concentrations such as to contain not more than 500 and not less than 5 γ. The shape of the chromatograms, developed by means of suitable reagents, is that of a circular band slightly elliptical because of the different diffusion rate of the mobile phase, higher following the grain of the paper; therefore, in order to calculate the values of R_F, the average of at least four values, measured along two orthogonal diameters, is necessary.

The disc, previously freed from the mobile phase, is sprayed with the solution of the appropriate reagent; thus a 1% solution of K_2CrO_4, taking care to eliminate the excess, treating it with sulphur dioxide gas, is suitable not only for the detection of Pb^{+2}, Ag^+, Tl^+, but also for the separation of these three components. Cu^{+2} ion is detected by a 0.2% solution of rubeanic acid in methyl alcohol which produces olive-green rings; but to separate it from Cd^{+2}, H_2S gas is used, the paper being previously neutralized with ammonia. Co^{+2} and Ni^{+2} are detected simultaneously by an alcoholic solution of rubeanic acid, alkalized with 0.1% of ammonia, from which Co^{+2} appears as a yellowish-brown ring and Ni^{+2} as a violet-blue. Ni^{+2} alone is detected by dimethylglyoxime (1% in C_2H_5OH), Pb^{+2} and Ba^{+2}, simultaneously, by spraying with 0.1% rhodizonic acid and then dilute hydrochloric acid, Pb^{+2} appearing as a violet and Ba^{+2} as a dark red ring.

According to the different concentrations the values of the R_F, found for the cation under examination are the following:

TABLE I

R_F VALUES

Pb^{+2}	0.16
Ag^+	0.24
Cu^{+2}	0.32
Cd^{+2}	0.21
Co^{+2}	0.20
Ni^{+2}	0.20
Tl^+	0.18

From the above values it is evident that for a mixture of Ag^{+}, Pb^{+2} and Tl^{+}, chromatographic separation is possible, which, however, given the proximity in the values of the two last, requires the mobile phase to be run rather longer than usual; for Co^{+2} and Ni^{+2} the identity of R_F does not allow a distinct separation, although a mixture of 5 parts of Ni^{+2} and 1 of Co^{+2} produces a chromatogram in which Ni^{+2} appears as a bluish-violet ring and Co^{+2} as a yellow one, outside the first; the separation Cu-Cd also is clear, as is seen from Fig. 3 (p. 333).

The variation in the photometric intensity of the bands, depending on the concentration, is recorded by densitometric measures. These are carried out with an optical densitometer, provided with a mirror galvanometer (10^{-9} A, 320 Ω). The optical system* easily set up, is composed of a 6 Volt, 3.4 Amp lamp, the beam of which strikes a mirror at an angle of 45°, which, through a slit made on a support provided with a micrometric screw, allows the reflexion of it on a Weston (Mod. 595) photocell, the sensitivity of which is adjusted by a potentiometer.

The apparatus is provided with: 1) an infinite-focus projector whose beam is adjusted on to the galvanometer mirror and from this reflected on the apposite scale, carrying transmittance and optical density marks; 2) a series of diaphragms to regulate the intensity of the beam; 3) a series of coloured filters to give the densitometric readings the maximum sensitivity.

The choice of the reagent to detect the ions under examination must not only allow a marked sensitivity, but, above all, must provide a fast colour, suitable for densitometric measurements, given the characteristics of the photoelectric cell.

Densitometric determinations are made in direct light, on filter paper stretched very taut and rendered transparent by a solution of appropriate refractive index, such as anysol (1.515) or a mixture of paraffin oil and α-bromonaphthalene.

The instrument is set up assuming that the optical density of the paper, taken at a point outside the ring, is equal to 0; the readings are taken at regular intervals, advancing the paper with an increase of 1 mm and making for every chromatogram a series of readings along two orthogonal diameters.

Such values make the construction of diagrams possible taking as abscissa the displacements in mm and as ordinate the corresponding values of optical density. The resulting curves, all having a maximum and a steep inclination, originate and end in two points corresponding to the optical density of the paper taken equal to 0.

In the following figure densitometric curves for decreasing concentrations are shown that, given the symmetry of the band, refer only to the photometry of two sections, cut from two orthogonal diameters and, given the analogy in the behaviour of the various ions, are limited to those of lead only (Fig. 1).

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* In the planning of the apparatus Ferrania S.A. has been very helpful, contributing also with the gift of part of the materials.

The area contained by the curve results as a triangle whose base corresponds to the width of the band, whose height corresponds to the maximum optical density and whose measure can be considered as the integer of the total optical density. The value of the area in cm², obtained with planimetric measurements and shown in the following table for the Pb^{+2}, Ag^{+} and Ni^{+2}, results from the average of the values of the four single densitometric areas:

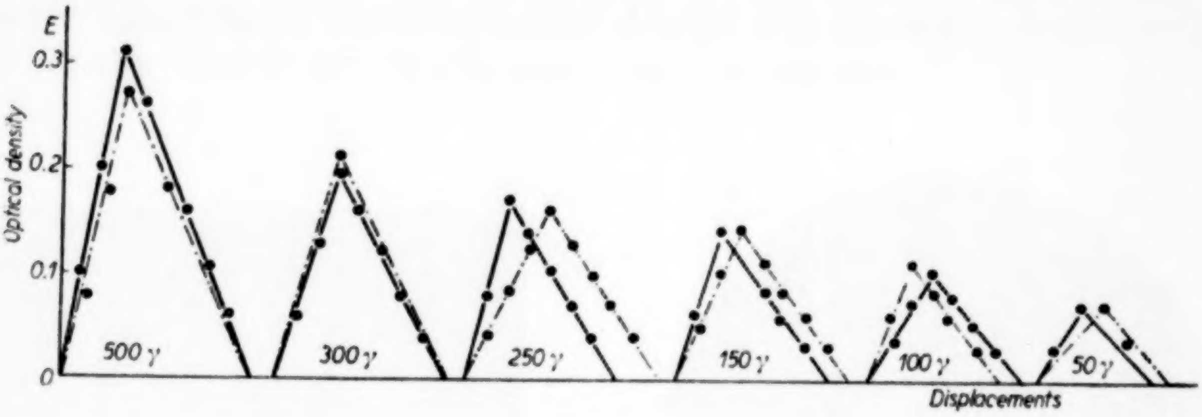

Fig. 1

TABLE II

DENSITOMETRIC AREAS

	500	300	250	150	100	50	40	10	5
Pb^{+2}	15.9	10.3	8.2	5.9	4.2	2.3	—	—	—
Ag^{+}	7.6	5.2	4	2.1	1.6	—	—	—	—
Ni^{+2}	—	—	—	17.3	11.7	7.4	5.2	2.2	—

Taking as abscissa the values of the concentration expressed in γ and as ordinate the values of the corresponding densitometric areas expressed in cm², the diagrams of the following figures are obtained (Fig. 2) from which results the linear relation between the concentration of the ions in the solutions and the total densitometric area. The formula connecting the optical density, D, to the concentration, c, is, therefore,

$$D = a.c$$

in which the value of a, different for each ion considered, corresponds to the inclination of the straight line. For the Pb^{+2} ion it is 0.0307, for the Ag^{+} 0.0176, for the Ni^{+2} 0.1333. The variation in the inclination of the straight line for the individual ions also depends on the nature and sensitivity of the reagent and, thence, on the type of colour measured, no less than on some intrinsic properties of the ion under examination, probably not the least being that of its ionic radius.

Observing the course of every single curve enclosing the triangular space, it is seen that the resulting triangle is not isosceles; the external side (reproducing densitometric values corresponding to the external edge of the band) has a rather strong inclination; the position of the maximum on the densitometric curve, in correspondence with the external part of the band, shows the increase in the number of the ions per unit area towards the external edge. This phenomenon is manifested from direct observation of the chromatogram in the form of a deepening of the colour towards the outside of the circular crown, as is evident from the photographic reproduction of a series of chromatograms made on decreasing concentrations of Pb^{+2}, Ni^{+2} and Ag^{+} (Fig. 4).

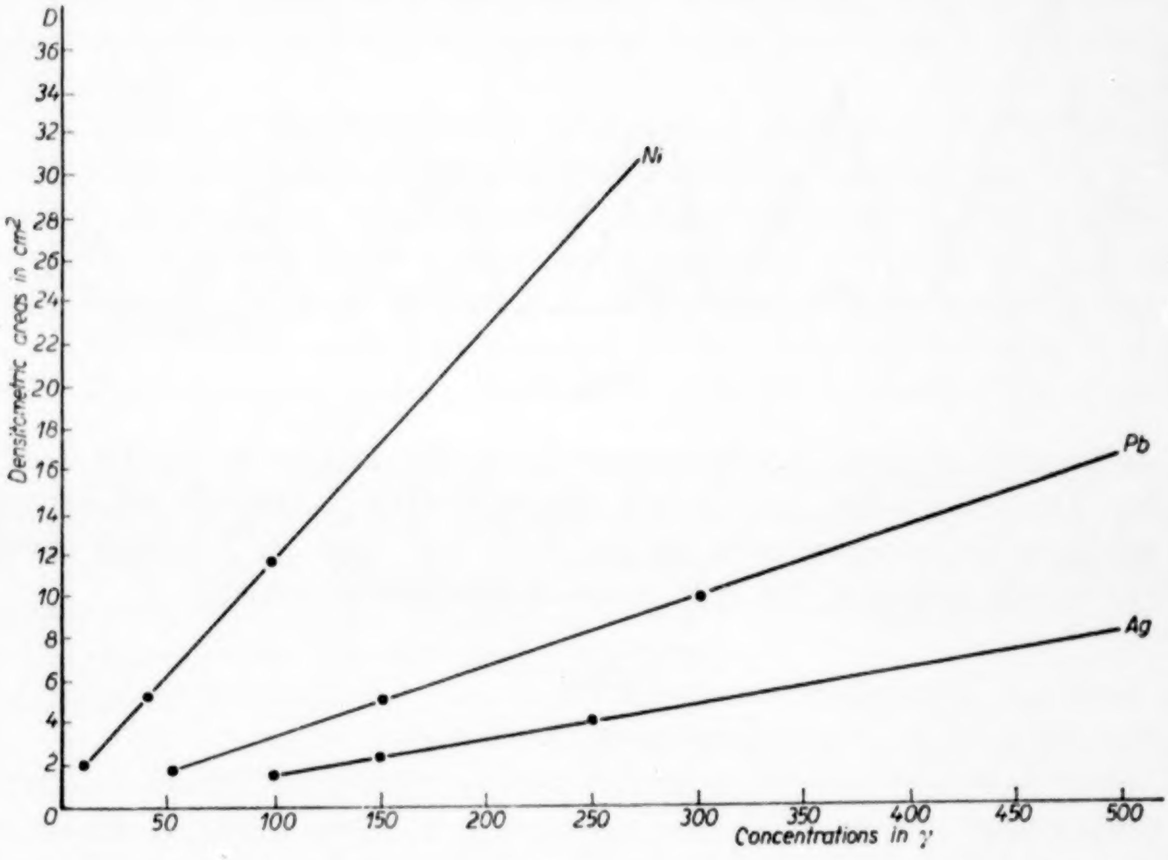

Fig. 2

In conclusion it can be said that, by means of radial inorganic chromatography on filter paper, a knowledge of the ionic concentration can be obtained, either by the measurement of the width of the band, or from that of the circular area corresponding to it, or from the total densitometric area; but while the measurement based on the first criterion does not provide any physical deduction as a function of the dimensions, the deduction of the concentration from the area (or rather from the logarithm of the latter) provides information about the density of the ions in the area, assuming however that the density is homogeneous. Since, on the other hand, the photometric curves have shown the variation of the optical density along the width of the band, according to a clearly defined outline, from the knowledge of the total optical density it is possible to calculate the concentration directly by the effective density of the ions.

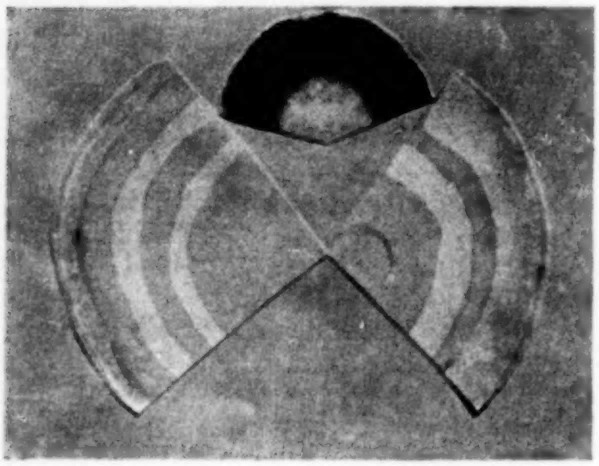

Fig. 3

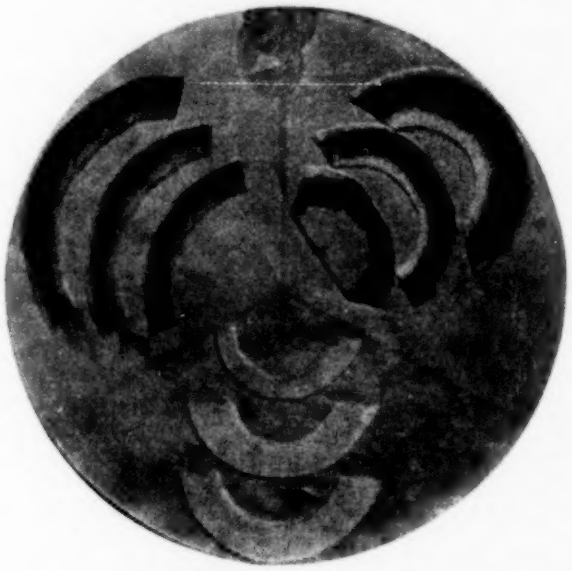

Fig. 4

The phenomenon of the increase in the number of ions per unit area, verified under the conditions of the experiment (and the more evident the phenomenon the greater is the concentration in the solution, and the greater the run under the action of the complex-forming mobile phase, benzoylacetone-butanol-nitric acid, which repels the ions radially), is not easy to explain; as far as the flow is concerned, it is worth noticing that the transport flow, stronger in the centre of the disc, corresponding to the spot's point of application, will tend to diminish with the displacement towards the outside, presumably according to the law $1/r^2$. Consequently the increase in the number of ions per unit area should have its maximum point towards the outside. Always bearing in mind only the extent of the complex-forming mobile phase, the increase in the number of ions on the external edge could be seen as a consequence of the removal and, hence, of the increasing denseness of an obstacle, driven by the flow towards the outside. But while the migration speed of the complex-forming mobile phase is to be considered as decreasing from the point of application towards the outside, the diffusion speed of the ions of the same type, although depending on the nature of the ion itself, is to be considered statistically constant. For this reason the radial migration speed of the ions, according to the decreasing speed of the

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mobile phase, would be smaller for those ions or complex molecules on the outside part of the circular band.

The interpretation of such a phenomenon is, doubtless, not easy, since it is logical to wonder whether, even if the same problem could be posed mathematically on the basis of analogies with the mechanics of fluids or with the theory of the flow of heat, such analogies can be applied to a phenomenon in which multiple forces are at work, some of which are as yet little known and of different natures, such as the phenomena of capillarity, of physical and chemical absorption, of the double layer, asymmetric and irregular disposition of the support, etc., which forces, acting simultaneously, may also do so in opposing directions.

SUMMARY

Radial chromatographic investigations carried out on various cations, using as complex-forming mobile phase a mixture of benzoylacetone-butanol-nitric acid, make it possible to establish a linear relation between the ionic concentration and the total optical density considering as such the triangular area enclosed by the densitometric curves. The position of the maximum of the latter shows an increase in the number of the ions towards the outside of the band, detectable also by direct observation of the chromatogram as a thickening of the colour.

RÉSUMÉ

Les auteurs ont effectué une étude de chromatographie circulaire pour divers cations, en utilisant comme réactif mobile complexant un mélange benzoylacétone-butanol-acide nitrique. Il est possible d'établir alors une relation linéaire entre la concentration ionique et la densité optique totale, considérant comme telle la surface triangulaire comprise dans les courbes densitométriques. La position du maximum de ces dernières met en évidence une augmentation de concentration des ions vers l'extérieur, visible aussi par observation directe du chromatogramme, sous forme d'une intensification de la coloration.

ZUSAMMENFASSUNG

Mit verschiedenen Kationen ausgeführte ring-chromatographische Untersuchungen, unter Benutzung einer Mischung von Benzoylaceton-Butanol-Salpetersäure als verbindungsformende Entwicklungsflüssigkeit, führten zur Feststellung eines linearen Verhältnisses zwischen der ionischen Konzentration und der gesamten optischen Dichte, wenn man als solche die dreieckige Fläche betrachtet. die von den densitometrischen Kurven eingeschlossen ist. Die Lage des Maximums der letzteren hebt die Verdichtung der Ionen nach der äusseren Zone des Rings zu hervor, was auch bei der direkten Beobachtung des Chromatograms als eine Verdichtung der Farbe zu sehen ist.

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PAPER CHROMATOGRAPHY OF ORGANOMETALLIC COMPLEXES: DITHIZONATES

by

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INTRODUCTION

The diphenylthiocarbazone, usually called "dithizone", is a coloured organic compound which forms yellow, red or violet interior complexes reacting with different metals, particularly with the metals classified in the sub-groups of the periodic system.

The dithizone exists in two forms: in the ketonic and in enolic form.

Large studies about its properties and its constitution were made by FISCHER[1] and, more recently, by IRVING and co-workers[2].

The more probable form of the complexes is the ketonic one, which is stable in acid or neutral solution. The following formulas may be assigned:

$$\mathrm{Me(I)\ (DH);\ Me(II)\ (DH)_2;\ Me(III)\ (DH)_3}$$

in which Me(I), Me(II), Me(III) are the metals, respectively a mono-, bi- or trivalent metal, and DH the keto-dithizone radical.

By treating the ketonic form with alkali we obtain the enolic one, with liberation of the dithizone.

The enolic form has the formula $\mathrm{Me(I)_2\ D}$ or Me(II) D, etc.
(D = radical of the enolic form).

The reaction may be represented by the following equation:

$$\mathrm{Me(II)\ (DH)_2 + 2\ (OH)^- \longrightarrow Me(II)\ D + 2\ H_2O + D^{-2}}$$

We have the inverse reaction in acid solution, with separation of metallic ions.

$$\mathrm{2\ Me(II)\ D + 2\ H^+ \longrightarrow Me(II)\ (DH)_2 + Me^{+2}}$$

The enolic form contains a greater quantity of metal and the ketonic one a greater quantity of dithizone.

In order to contribute to the study of the metallic dithizonates, we made some systemical investigations into the chromatographic behaviour of these compounds at different pH and with different solvents. Successively we proceed to their separation.

We executed the chromatography on filter-paper, which proved to be more suitable for obtaining the desired results.

As to the experimental technique, we adopted a device similar to the one used by LASKOWSKI AND MCCRONE[3]. We used the same technique, with the suitable modifications, in a previous investigation[4].

The filter-paper was treated with buffer solutions, having pH values from 1 to 10, prepared according to the series of KLARK AND LUBS[5].

The pH was controlled by means of a Leeds-Northrup potentiometer (glass-calomel electrode).

The composition of the buffer solutions are given in the following Table I.

TABLE I

COMPOSITION OF THE BUFFER SOLUTIONS

pH	Molarity and proportions of the components
1	50 ml KCl (0.2*M*) + 97 ml HCl (0.2*N*) → 200 ml
2	50 ml KCl (0.2*M*) + 10.6 ml HCl (0.2*N*) → 200 ml
3	50 ml potassium diphthalate (0.1*M*) + 20.32 ml HCl (0.1*N*) → 100 ml
4	50 ml potassium diphthalate (0.1*M*) + 0.40 ml NaOH (0.1*N*) → 100 ml
5	50 ml potassium diphthalate (0.1*M*) + 23.85 ml NaOH (0.1*N*) → 100 ml
6	50 ml KH_2PO_4 (0.1*M*) + 5.70 ml NaOH (0.1*N*) → 100 ml
7	50 ml KH_2PO_4 (0.1*M*) + 29.63 ml NaOH (0.1*N*) → 100 ml
8	50 ml H_3BO_3 (0.1*M* in 0.1*M* KCl sol.) + 3.97 ml NaOH (0.1*N*) → 100 ml
9	50 ml H_3BO_3 (0.1*M* in 0.1*M* KCl sol.) + 21.30 ml NaOH (0.1*N*) → 100 ml
10	50 ml H_3BO_3 (0.1*M* in 0.1*M* KCl sol.) + 43.90 ml NaOH (0.1*N*) → 100 ml

The experiences were made also on paper not previously treated with buffer solution.

We used Whatman No. 1 filter-paper having the following dimensions: cm 6 × 50.

The filter-paper, rolled up, was immersed for 7 hours in 100 ml beaker containing the buffer solution.

After drying for about 12 hours in ambient air, thinner bands were cut again (dimensions: cm 1 × 25).

The dithizonates were chromatographed on these paper bands.

We took into consideration the complex compounds of the dithizone with the following metals: Ag, Hg, Zn, Cu, Cd, Pb, Bi.

The Ag and Hg complexes were prepared with the IRVING and co-workers' technique[2]. The other compounds were obtained from corresponding nitrates with 1.5‰ dithizone solution in chloroform, at its "optimum" extraction pH[6].

After evaporating and purifying, the dithizonates were in the form of crystalline powders, red-brown in colour, except copper dithizonate, which is black with greenish reflections.

We chromatographed each time 0.01 ml of $M/100$ solutions in chloroform of complexes of Zn, Cu, Ag, Bi and respectively of $M/500$ solutions of Pb, Cd, Hg dithizonates. The solutions were run from a microburette at about 3 cm from the beginning of the chromatograms.

We used as solvents a series of aliphatic alcohols with simple or ramified chain, with increasing number of C atoms, from methyl to *iso*-amyl alcohol; more exactly: methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, amyl, *iso*-amyl alcohols. The experimental temperature was 27° C (± 2° C).

We obtained variously coloured bands, as is shown in Table II, where the colours of the different dithizonates are specified.

The bands were sometimes linear, sometimes diffused.

TABLE II

COLOURS OF THE DIFFERENT DITHIZONATES

Dithizonates	colour
ZnDz	red — violet
CdDz	yellow — red
HgDz	yellow — orange
BiDz	brown
PbDz	pink
CuDz	brown — green
AgDz	brown — red

EXPERIMENTAL RESULTS

Behaviour of the single dithizonates

The results obtained with the different dithizonates are summarized in the Table III, IV, V. In Table III the variation of the R_F values of the dithizonates with increasing of the buffer solution pH is shown: the solvent was methyl alcohol.

In Fig. 1 we have traced the diagram corresponding to the behaviour of the Zn, Cd, Hg, Pb dithizonates.

The R_F values of Zn, Cd, Hg dithizonates versus pH present a lowering at pH 3, increase continuously up to pH 7 and decrease in basic solution.

TABLE III

R_F VALUES OF THE DITHIZONATES VERSUS THE PH OF THE BUFFER SOLUTION METHYL ALCOHOL USED AS SOLVENT

pH	1	2	3	4	5	6	7	8	9	10	not buffered paper
ZnDz	0.54	0.57	0.50	0.65	0.72	0.76	0.77	0.73	0.68	0.55	0.63
CdDz	0.59	0.62	0.57	0.60	0.66	0.72	0.81	0.80	0.75	0.66	0.66
HgDz	0.40	0.43	0.28	0.54	0.60	0.64	0.69	0.65	0.63	0.50	0.58
PbDz	0.71	0.66	0.69	0.75	0.75	0.75	0.75	0.74	0.66	0.60	0
CuDz	0	0	0	0	0	0	0	0	0	0	0
AgDz	0	0	0	0	0	0	0	0	0	0	0

The R_F values of the Cu and Ag dithizonates remain the same ($R_F = 0$) in the entire pH range. The R_F values of the Pb dithizonates are intermediate between 0 and 1; the maximum corresponds to pH = 4 and the diagram line decreases in basic solution.

On filter-paper not treated with buffer solution the Pb dithizonate has $R_F = 0$; the same value was observed with all the other alcohols having a greater number of C atoms. The diagram shows that in acid solution the R_F values corresponding to the same pH are quite different, while they are closer together in acid solution.

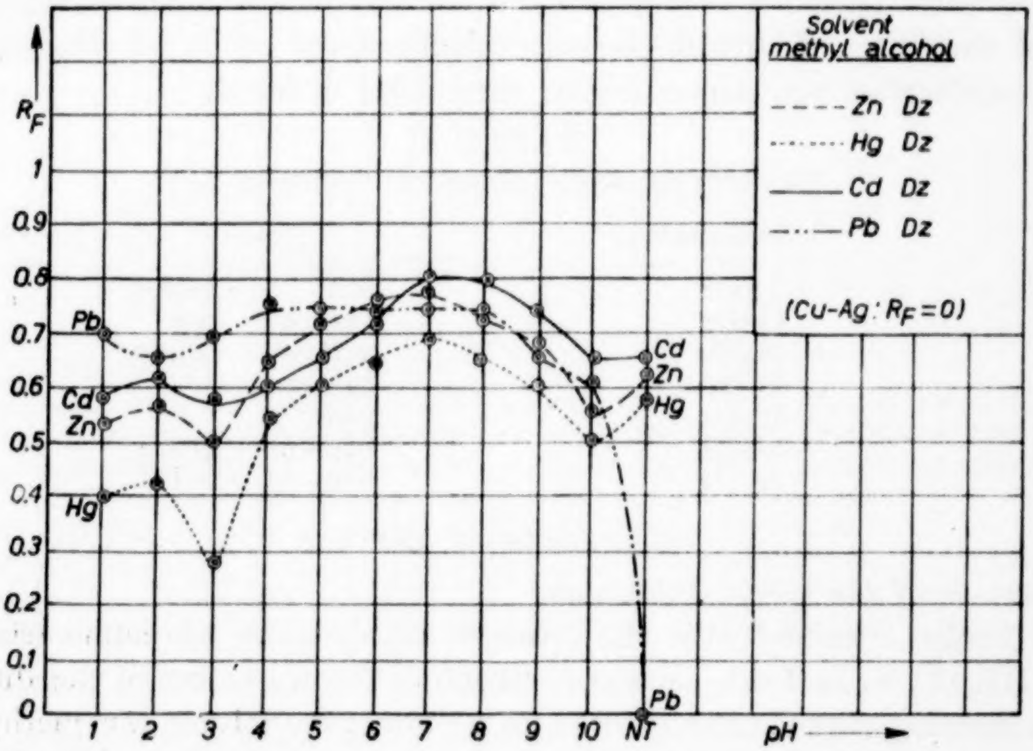

Fig. 1

It is possible to state that in this zone the separations can be made more easily, in absence of accessory actions concerning the stability of the complexes.

We cannot determine the R_F value of the Bi dithizonate with methyl alcohol, because with this alcohol it presents a diffuse band from the origin to the advancing front of liquid. The same behaviour is noticed with ethyl alcohol. On the contrary, with these alcohols, in some binary separations, $R_F = 1$ and a good separation from dithizonates with $R_F = 0$ is possible.

In Table IV the behaviour of the different dithizonates is summarized, when ethyl alcohol is used as solvent.

The Ag, Cu, Pb dithizonates do not move from the origin, while the Zn, Cd, Hg dithizonates have their R_F closer to the advancing front of liquid, especially in basic solution; however, in some zones of pH they show an intermediate beha-

TABLE IV

R_F VALUES OF THE DITHIZONATES VERSUS THE PH OF THE BUFFER SOLUTION ETHYL ALCOHOL USED AS SOLVENT

pH	1	2	3	4	5	6	7	8	9	10	not buffered paper
ZnDz	0.49	0.75	0.82	0.93	0.95	1	1	1	1	1	1
CdDz	—	0.64	0.73	0.82	0.89	0.93	1	1	1	1	1
HgDz	0.31	0.66	0.75	0.88	0.91	0.95	1	1	1	1	1
PbDz	0	0	0	0	0	0	0	0	0	0	0
CuDz	0	0	0	0	0	0	0	0	0	0	0
AgDz	0	0	0	0	0	0	0	0	0	0	0

viour, like the behaviour presented in methyl alcohol. The corresponding diagrams are represented in Fig. 2.

We can notice that in acid solution the R_F of Hg, Cd, Zn dithizonates have increasing values up to $R_F = 1$, at pH 7.

They are, however, closer together than in methyl alcohol. It is easy to foresee a greater difficulty in the separation.

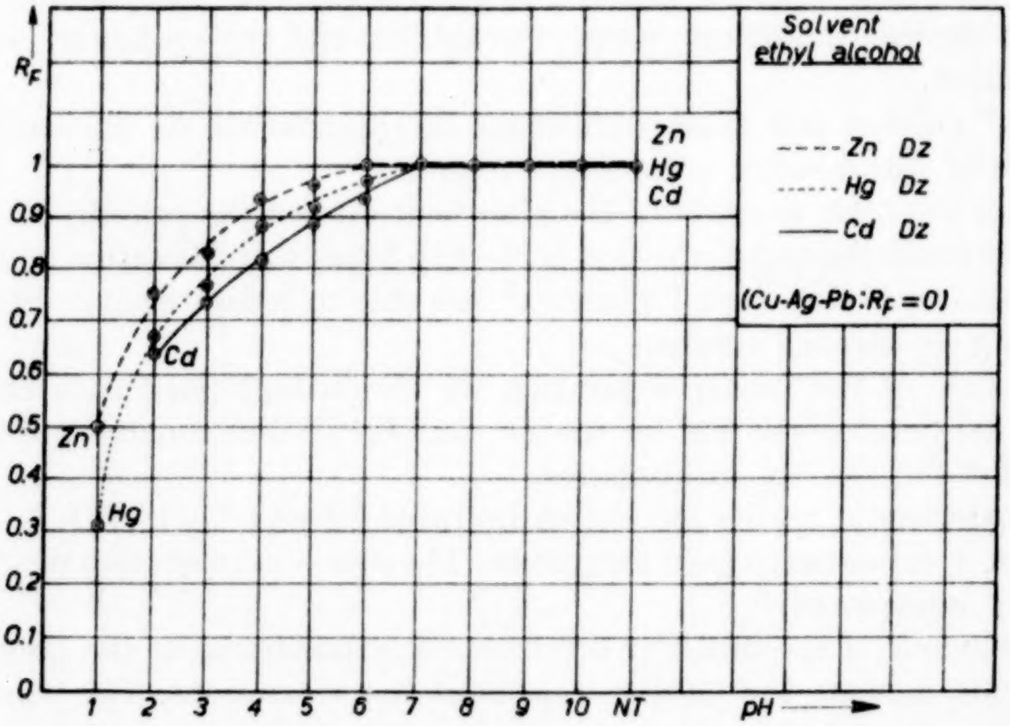

Fig. 2

In basic solution, all the Hg, Cd, Zn dithizonates have the value $R_F = 1$ (no separation is possible). They have the same value in the whole range of pH, also with alcohols having a greater number of C atoms, see Table V, where the R_F values with *n*- and *iso*-propyl, *n*- and *iso*-butyl, *n*- and *iso*-amyl alcohols are shown.

The Pb, Cu, Ag dithizonates do not move from the origin, while the Zn, Cd, Hg, Bi dithizonates reach the advancing front of liquid.

TABLE V

R_F VALUES OF THE DITHIZONATES VERSUS THE PH OF THE BUFFER SOLUTION *n*- AND *iso*-PROPYL, *n*- AND *iso*-BUTYL, *n*-AND *iso*-AMYL ALCOHOLS AS SOLVENTS

pH	from 1 to 10	paper not treated with buffer solution
ZnDz	1	1
CdDz	1	1
HgDz	1	1
BiDz	1	1
PbDz	0	0
CuDz	0	0
AgDz	0	0

Binary separations of the dithizonates

After the observation of the behaviour of each dithizonate, we proceed to their separations.

These separations presented some difficulties in relation with the very closed molecular constitution of the metallic complexes and with the possible transformation of the two tautomeric forms, the ketonic and the enolic one, in acid or basic solution.

WILSON[7] pointed out these difficulties in experiments on chromatographic separation of dithizonates on alumina column.

Probably the basic reaction of the adsorbent altered the primitive conditions of pH, and caused the transformation of the two forms with liberation of dithizone.

However, in previous work ERÄMETSA[8] was able to separate some dithizonates by working on alumina column.

In the case of the binary separation we chromatographed each time 0.005 ml of $M/100$ titrated solution for the Zn, Cu, Ag, Bi dithizonates and of $M/500$ solution for Pb, Cd, Hg dithizonates.

The experimental results are shown in Table VI and Table VII.

The sign + represents a good separation. The sign — a separation which cannot be exactly interpreted.

The behaviour of the different dithizonates, summarized in the previous diagrams, could indicate the positive results of the separations. The bands of the dithizonates showed the same colours obtained in the single chromatograms, with intermediate R_F values in the case of methyl and ethyl alcohols, and $R_F = 0$ or $R_F = 1$ in the case of superior alcohols.

Ternary separations

We try to execute the ternary separations with methyl and ethyl alcohols. On the basis of the previous results, with these alcohols only is it possible to foresee good separations.

TABLE VI

BINARY SEPARATIONS OF THE DITHIZONATES

Solvent: methyl alcohol

Dithizonates	pH										not buffered paper
	1	2	3	4	5	6	7	8	9	10	
Ag - Zn	+	+	+	+	+	+	+	+	+	+	+
Cu - Zn	+	+	+	+	+	+	+	+	+	+	+
Hg - Zn	+	+	+	+	+	+	—	+	+	+	+
Ag - Hg	+	+	+	+	+	+	+	+	+	+	—
Ag - Bi	+	—	—	—	—	—	—	+	—	—	—
Cu - Bi	+	—	—	—	—	—	—	—	—	—	—
Ag - Pb	—	+	+	—	—	—	—	—	—	—	—
Hg - Pb	—	—	+	—	+	—	—	—	—	—	—

Solvent: ethyl alcohol

Dithizonates	pH										not buffered paper
	1	2	3	4	5	6	7	8	9	10	
Ag - Zn	+	+	+	+	+	+	+	+	+	+	+
Cu - Zn	+	+	—	+	—	—	—	+	+	+	+
Ag - Hg	—	+	+	+	+	+	+	+	—	—	+
Ag - Bi	—	+	+	+	+	+	+	+	+	—	+
Cu - Pb	—	+	—	—	—	—	—	—	—	—	—
Cu - Bi	—	+	—	—	+	—	—	—	—	—	—

Solvent: propyl alcohol

Dithizonates $R_F = 0$ $R_F = 1$	pH										not buffered paper
	1	2	3	4	5	6	7	8	9	10	
Ag - Zn	+	+	+	+	+	+	+	+	+	+	+
Cu - Zn	+	—	—	—	—	—	—	+	+	+	+
Ag - Hg	—	+	+	+	+	+	+	+	+	+	+
Ag - Bi	+	+	+	+	+	+	+	+	+	+	+
Cu - Bi	+	+	—	+	+	+	+	+	+	+	—
Pb - Hg	—	+	+	—	+	—	—	—	—	—	—
Pb - Bi	—	—	+	—	—	—	—	—	—	—	—

Solvent: *iso*propyl alcohol

Dithizonates $R_F = 0$ $R_F = 1$	pH										buffered paper not
	1	2	3	4	5	6	7	8	9	10	
Ag - Zn	+	+	+	+	+	+	—	—	+	+	+
Cu - Zn	+	+	—	—	—	—	—	+	+	+	+
Ag - Hg	—	—	+	+	+	+	—	—	—	—	—
Ag - Bi	—	+	+	+	+	+	+	+	+	+	+
Cu - Bi	—	+	—	+	+	+	+	+	+	+	—
Pb - Bi	—	+	+	—	—	—	—	—	+	—	—
Pb - Hg	—	—	+	—	—	—	—	—	—	—	—

TABLE VII

BINARY SOLUTIONS OF THE DITHIZONATES

Solvent: butyl alcohol

Dithizonates		pH										not buffered paper
$R_F=0$	$R_F=1$	1	2	3	4	5	6	7	8	9	10	
Ag -	Zn	+	+	+	+	+	+	+	+	+	+	+
Cu -	Zn	+	+	+	—	—	—	—	+	+	+	+
Ag -	Hg	—	+	+	+	+	+	+	+	+	+	+
Ag -	Bi	+	+	+	+	+	+	+	+	+	+	+
Cu -	Bi	+	+	+	+	+	+	+	+	+	+	—
Cu -	Hg	—	+	+	—	—	—	—	—	—	—	—

Solvent: *iso*butyl alcohol

Dithizonates		pH										not buffered paper
$R_F=0$	$R_F=1$	1	2	3	4	5	6	7	8	9	10	
Ag -	Zn	+	+	+	+	+	+	+	+	+	—	+
Cu -	Zn	+	—	+	+	+	—	—	+	+	+	+
Ag -	Hg	—	+	+	+	+	+	+	+	+	+	+
Ag -	Bi	+	+	+	+	+	+	+	+	+	+	+
Cu -	Bi	+	+	+	+	+	+	+	+	+	+	+
Pb -	Bi	—	+	+	—	—	—	—	+	—	—	—
Pb -	Hg	—	+	+	—	—	—	—	—	—	—	—
Cu -	Hg	—	—	+	—	—	—	—	—	—	—	—

Solvent: amyl alcohol

Dithizonates		pH										not buffered paper
$R_F=0$	$R_F=1$	1	2	3	4	5	6	7	8	9	10	
Ag -	Zn	+	+	+	+	+	+	+	+	+	+	+
Cu -	Zn	+	+	—	—	—	—	—	+	+	+	+
Ag -	Hg	—	+	+	+	+	+	+	+	+	+	+
Ag -	Bi	+	+	+	+	+	+	+	+	+	+	+
Cu -	Bi	+	+	+	+	+	+	+	+	+	+	+
Pb -	Hg	—	—	+	—	—	—	—	—	—	—	—
Cu -	Hg	—	—	+	—	—	—	—	—	—	—	—

Solvent: *iso*amyl alcohol

Dithizonates		pH										not buffered paper
		1	2	3	4	5	6	7	8	9	10	
Ag -	Zn	+	+	+	+	+	+	—	+	+	+	+
Cu -	Zn	+	+	+	—	—	—	—	+	+	+	+
Ag -	Hg	—	+	+	+	+	+	+	+	+	+	+
Ag -	Bi	+	+	+	+	+	+	+	+	+	+	+
Cu -	Bi	+	+	+	+	+	+	+	+	+	+	+
Pb -	Bi	—	+	+	—	—	—	—	—	—	—	—
Pb -	Hg	—	—	+	—	—	—	—	—	—	—	—
Cu -	Hg	—	—	+	—	—	—	—	—	—	—	—

The experiments are summarized in Table VIII.

TABLE VIII

TERNARY SEPARATIONS

Dithizonates	Solvent	pH 1	2	3	4	5	not buffered paper
Ag-Hg-Zn	Methyl alcohol	+	+	+	+	+	+
Ag-Hg-Zn	Ethyl alcohol	+	+	—	—	—	—

In Fig. 3 the aspect of a ternary chromatogram is shown.

The order of displacement of the dithizonates from the origin is the following:

AgDz — HgDz — ZnDz.

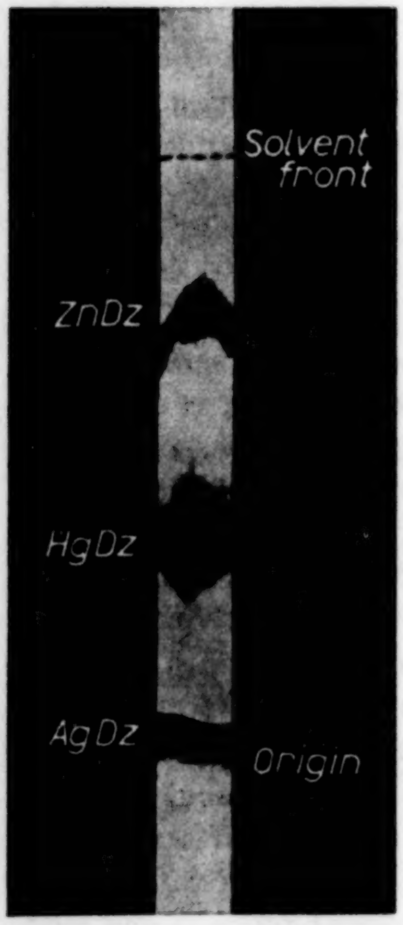

Fig. 3

DISCUSSION

Single dithizonates

The factors which have influence over the R_F values of the dithizonates are the following: solubility of these compounds in the different alcohols, pH of the buffer solution (for the methyl and ethyl alcohols the R_F values are placed on a definite curve line, considering the different buffer solutions used in order to have the pH increasing from 1 to 10), salts present in the buffer solution, different partition coefficient which each time is established between the buffer solution and the alcohol, saturation conditions, experimental temperature and so on.

We can remark that R_F values of Zn, Cd, Hg dithizonates increase with the pH and with the increasing number of the carbon atoms in the solvent alcohol; moreover, we can observe, with all alcohols, an analogous behaviour, of the dithizonates of metals which are classified in the same sub-group of the same group in the periodic system (Zn, Cd, Hg dithizonates and Ag, Cu dithizonates).

A concurrent action (pH of the buffer solution — solvent alcohol) influences the stability of the dithizonates. In the case of Zn dithizonate the optimum of the stability (unaltered colour) corresponds to pH values 8, 9, 10 with all the alcohols. With Hg dithizonate the optimum corresponds to pH values from 4 to 9 with all the solvents except methyl alcohol; with this alcohol we noticed a certain stability for pH 6 and

8. Cd dithizonate has the optimum at pH 9 and 10 with almost all the alcohols. The same for the Pb dithizonate. The Ag and Cu dithizonates are stable over the whole pH range, with all the alcohols; Bi dithizonate only with superior alcohols.

The unusual behaviour of some dithizonates presenting a double band, respectively with $R_F = 0$ and $R_F = 1$, can be observed. It is peculiar to the Cu dithizonate with ethyl and superior alcohols in the entire pH range, except in strongly acid solution (pH 1-2) and for Ag dithizonate, having a double band with all the alcohols at pH from 4 to 10. The same behaviour is noticed in the case of the Zn dithizonate with *n*- and *iso*-butyl alcohols in all the pH conditions, with *n*- and *iso*-propyl alcohols, *n*- and *iso*-amyl alcohols specially in basic solution (pH 7-10) or at pH = 1.

We can think that the hydrochloric acid at the buffer solutions forms with the water a band preceding the solvent. They are two advancing fronts of two different liquids: the fraction having $R_F = 1$ is transported by hydrochloric acid and water and the other one remains at $R_F = 0$ because it is not removed by alcohol. Furthermore the presence of dithizone (formed by beginning decomposition of the dithizonates in basic solution) can form a band at the advancing front of liquid. The intensity of the band is increased in the presence of traces of iron in the filter-paper.

In the positive binary separations we have not these double bands.

Separations

The R_F values found in the binary separations are not exactlythe same as those found for the single dithizonates: however, the dispacement order is observed.

As to the "optimum" of our experiences, the binary separations of the Zn dithizonate are possible with methyl alcohol at all the pH values: the AgDz — ZnDz separation also with all the alcohols; the HgDZ — ZnDz separation is impossible with superior alcohols because we have the same value $R_F = 1$ for the two dithizonates.

For the same reasons the CuDz — ZnDz separation is possible with superior alcohols only under very acid conditions (pH 2-3) or in basic solution (pH 8, 9, 10).

AgDz and HgDz separate under all the pH conditions (except pH = 1) and with all the alcohols, while AgDz and PbDz only in strongly acid solution (pH 2-3) and with methyl alcohol (in this case the Pb dithizonate has $R_F \neq 0$). The HgDz — PbDz separation (very difficult to determine in relation with the likeness in the colour of these two compounds) is easier at pH = 3 and with superior alcohols.

We can point out that the value pH = 3 permits the greatest number of separations, especially with superior alcohols.

The fact could derive from the composition of the buffer solution and moreover this pH value probably represents the "optimum average" for the stability of the dithizonates that we have considered.

SUMMARY

The chromatographic behaviour of the dithizonates of Zn, Cd, Hg, Bi, Pb, Cu, Ag has been studied by using the filter-paper treated with different buffer solutions (pH from 1 to 10) and a series of the aliphatic alcohols (from the methyl to *iso*-amyl alcohol) as developing solvents.

The binary and ternary separations of the above-mentioned complexes have been made. It has been observed that the dithizonates of the metals that are classified in the same sub-group of the same group of the periodic system behave analogously.

RÉSUMÉ

Les auteurs ont étudié le comportement chromatographique des dithizonates de Zn, Cd, Hg, Bi, Pb, Cu, Ag sur papier tamponné à différents pH (1 à 10), en employant comme solvants, pour développer les chromatogrammes, les alcools de la série aliphatique (méthylique à *iso*-amylique).

Ensuite, ils ont effectué les séparations binaires et ternaires de ces composés organométalliques; on peut remarquer une analogie de comportement entre les dithizonates des métaux d'un même sous-groupe du système périodique.

ZUSAMMENFASSUNG

Das chromatographische Verhalten der Dithizonate von Zn, Cd, Hg, Bi, Pb, Cu, Ag, auf mit Pufferlösung behandelten Filterpapier (mit verschiedenem pH von 1 bis 10) wurde bei Verwendung einer Reihe aliphatischer Alkohole (Methylalkohol bis *Iso*amylalkohol) untersucht. Zweifache und dreifache Trennungen obenerwähnter Komplexe wurden durchgeführt. Es wurde ein analoges Verhalten der Dithizonate der Metalle festgestellt, die derselben Untergruppe einer gleichen Gruppe des periodischen Systems angehören.

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AN ADSORPTION METHOD FOR SEMIQUANTITATIVE DETERMINATION OF COLOURED MATERIALS IN VERY DILUTE SOLUTION

by

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Although there are convenient methods for semiquantitative determinations of trace components, a lack is still felt of one by which different concentrations of coloured materials, diluted to such an extent that for the human eye and for most photosensitive receivers their solutions are colourless, could be determined semiquantitatively and colorimetrically. The concentrations which correspond to these dilutions are mostly less than 10^{-5} per cent. by weight of the coloured material. In our previous paper[1] we suggested as a solution to this problem that, by means of the isothermal equilibrium adsorption, the coloured material from such dilute solutions should be concentrated on an adsorbent of a limited surface area which was, by special process[2], given the form of a film. By photometric measurements on the reflected light, after the adsorption of the visibly coloured surface of the adsorbent, and making use of the reference curves obtained by the same process, it is possible to determine the unknown concentration.

The fundamental theoretical statement, which was made use of in our treatment of this question, was the well-known fact that the quantity of equilibrium adsorbed matter is a function of the concentration. It was only colorimetrically that we could compare the very small weight of the coloured material adsorbed. We were unable to carry out any check of the results obtained because to our knowledge there is no method at present (except, perhaps, the very inconvenient concentration by evaporation or the method of tracers) by which the equilibrium concentration of the coloured material remaining in the solution after the adsorption could be determined. On account of the high light absorption during its passage through the adsorbent, our colorimetric measurements were not made in transmitted — but in reflected light, for which reason we were unable to apply with sufficient exactness the law of Lambert-Beer[3].

Although we have arrived at this method by quite independent work, in the course of studying adsorption, it involves certain elements which had previously been used in some analytical methods. The basic characteristics of this method are: the establishment of the adsorption equilibrium under dynamic adsorption

conditions on an adsorbent of a limited surface area and thickness, obtained by a special procedure; direct colorimetric measurement of the surface of the adsorbent in diffusely reflected light. The analytical methods which involve some of the above-mentioned characteristics, according to the literature we have studied, would be those of YAGODA[4,5] and of CLARCE AND HERMANCE[6].

EXPERIMENTAL WORK

Working technique

In the treatment of this method methylene blue (medicinal) was used as the indicator and distilled water as a solvent. In most cases the concentrations range in the interval from 0.0000001 to 0.00001 % by weight and we obtained them by a gradual dilution of the original solution. Silica gel, prepared according to HARRIS AND WICK'S[7] directions, was used as an adsorbent. In order to obtain a good suspension for spraying and an active film for adsorption, first 15 ml of acetone and then 1 ml of 10% cellulose nitrate solution were added to 0.5 g of silica gel, previously dried and screened through a sieve No. 100 DIN 1171.

In our previous communication the process planned for the formation of the adsorbent film did not quite satisfy us and for that reason we had to resort to a less satisfactory solution of our problem, *i.e.* spraying a prepared suspension of silica gel over a porous foundation, which would give it the required mechanical resistance. As a base in our case we have chosen the filter-paper for quantitative filtrations (J. M. Munktell No. 004 ø = 9 cm) which, as an adsorbent, has much less affinity for methylene blue than silica gel, on account of which it was adsorbed mainly on this adsorbent. We cut the thus obtained complex: adsorbent film + filter-paper into little rounds 12 mm in diameter and with adsorbent side turned to the fresh solution carried out the adsorption in a special apparatus.

In order to have the same dynamic conditions it was necessary that the flow rate of the solution through the adsorbent be identical in the tests which are compared. This was achieved by the use of little adsorbent discs which had to be of the same porosity as to offer equal resistances during the passage of the solution. We got uniform adsorbent discs, with regard to their adsorptive abilities and porosity, by the simultaneous spraying, with the same suspension, of several rounds of filter paper and at the same time slowly revolving the base with the samples. The samples, *i.e.* the parts of the surface area of the filter paper that were the most homogeneously shaded, were selected, gently rubbed with another adsorbent to diminish their roughness, and cut out into little adsorbent discs for the individual series. On the other hand identical porosities of the adsorbent required the levels of the solution to be at the same height above each adsorbent and as high as to allow satisfactory flow rate, which should be identical for each single case in the same series. This condition was fulfilled by the use of a long (1 m) and comparatively thin (ø = 8 mm) tube, which broadened at its upper end (Fig. 1). To the lower end, by means of a piece of rubber tubing, we attached a hollow brass nut into which, between its plain surfaces, the absorbent film could be well tightened. In the same way as YAGODA[4] we obtained a completely limited adsorbent surface, the only one through which the solution could flow.

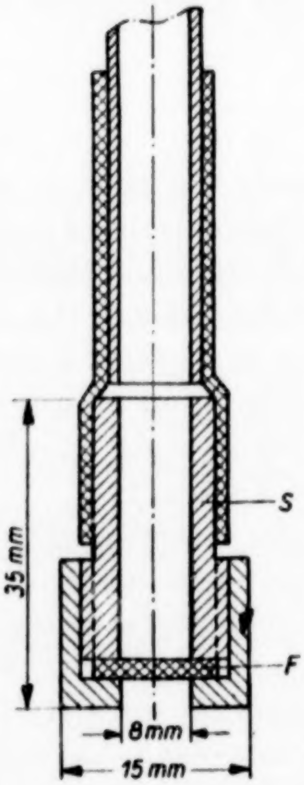

Fig. 1. Lower part of the adsorption tube
S Hollow bolt with its nut
F Little disc of adsorbent

In the course of our fundamental experiments we worked with 100 ml of the solution. A period of about 3 hours was necessary for this volume of solution to flow through the adsorbent. We worked with six concentrations simultaneously.

In order to establish the adsorption equilibrium on silica gel we followed the adsorption by noting the coloration intensity changes. It was necessary to pass the same solution through the adsorbent twice. For safety we passed it through the adsorbent three times which, on the grounds of good reproducibility, in all cases could be considered as quite sufficient. Therefore the total duration of the adsorption time amounted to about 9 hours.

When working with such low concentrations and at the same time with great concentration intervals, it is necessary to take into consideration adsorption, *viz.* the desorption of the coloured material from the surfaces of the apparatus and of the vessels with which the solution comes into contact. There exist two possibilities of doing this: either to carry out a preliminary feeding of the apparatus with successive fresh quantities of the original solution, before determination, till the adsorption equilibrium is established with respect to it and only then to introduce the solution by means of which the concentration is determined, or to introduce the original solution, without any previous saturation of the surface, into a quite clean apparatus. We decided upon the latter process, because in that case a smaller quantity of the original solution is necessary, the adsorption saturation at the contact surface (which is difficult to determine) need not be reached and, finally, the most important reason being that the liquid used passes through the apparatus three consecutive times. As the concentration of the coloured material, owing to an excellent adsorption on silica gel, was considerably smaller on its repeated regression into the apparatus, on its repassing, the coloured matter that had been adsorbed on the walls of the apparatus was desorbed and thus came into contact with the adsorbent.

Adsorption being completed, the adsorbent was taken out of the nut and dried in the air, avoiding direct sunlight (on account of a certain instability of this colour against stronger light sources), determined colorimetrically in diffusely reflected light in a colorimeter constructed specially for this case[8]. In order to have a constant voltage of the current flowing through the light source (which had proved to be a very important thing), the current should be taken from a set of lead accumulators of somewhat greater capacity. It is useful that this current, too, be taken potentiometrically, keeping voltage at a constant value by means of a sensitive voltmeter. The diagram of the entire arrangement is shown in Fig. 2.

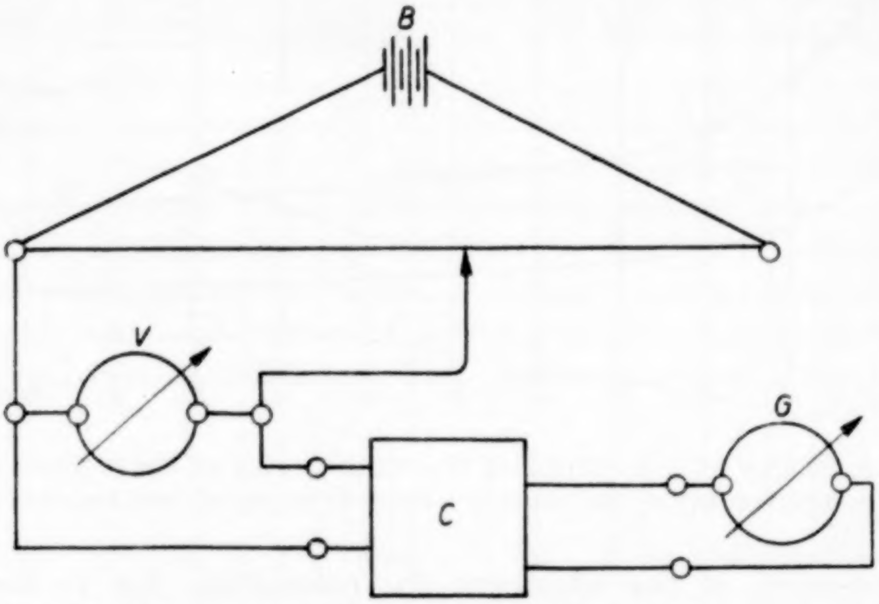

Fig. 2. The arrangement for colorimetric measurements
B Set of lead accumulators
C Colorimeter
G Galvanometer
V Voltmeter

RESULTS OF MEASUREMENTS

In our opinion, the only possible way of exact and applicable verification of the suggested method, using the above-mentioned working technique, is to illustrate the results obtained graphically in order to determine deviations of the points from the probable curve. It is desirable to get a straight, instead of a curved line, because the former is determined by a minimum number of points. The graphs were obtained by plotting solution concentration percentages on the abscissa and on the ordinate the photocurrent magnitudes in 10^{-9} amp., obtained by colorimetric measurement of the corresponding adsorbent rounds. Two such diagrams are shown in Fig. 3 in which the upper graph was obtained when the light source was fed by a voltage of 6 V while the current voltage of the lower one was 5 V. From the graphs may be seen that the deviations from the probable curve are greater for lower than for higher concentrations. The points of the lowest concentrations mostly fall under the curve, which means that they are more intensely coloured than they should be. According to our opinion this comes from the fact that even the smallest quantities of foreign coloured materials in the solution such as dust, copper salts (from brass screws), the colour from the rubber, considerably influence the colorations of the adsorbent, which for the lowest concentrations are themselves extremely faint. With the increase of the coloration intensity of the adsorbent the colorations due to these impurities relatively decrease giving thus better agreement in the case of higher concentrations.

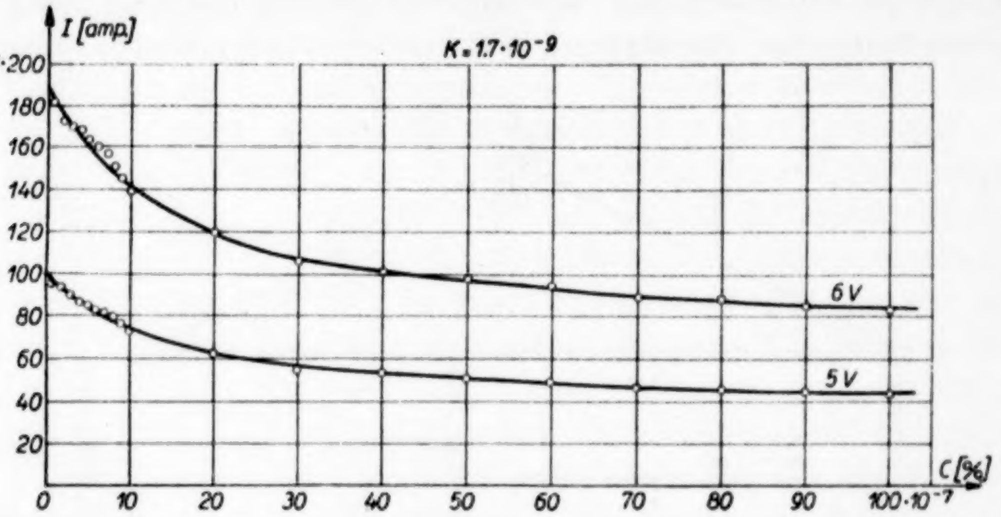

Fig. 3. The intensity of coloration of the same series of little discs of silica gel in dependence upon the initial concentration of methylene blue.

Judging from the mutual positions of the two illustrated curves we can see what a great effect the light has on the magnitude of the photocurrent in spite

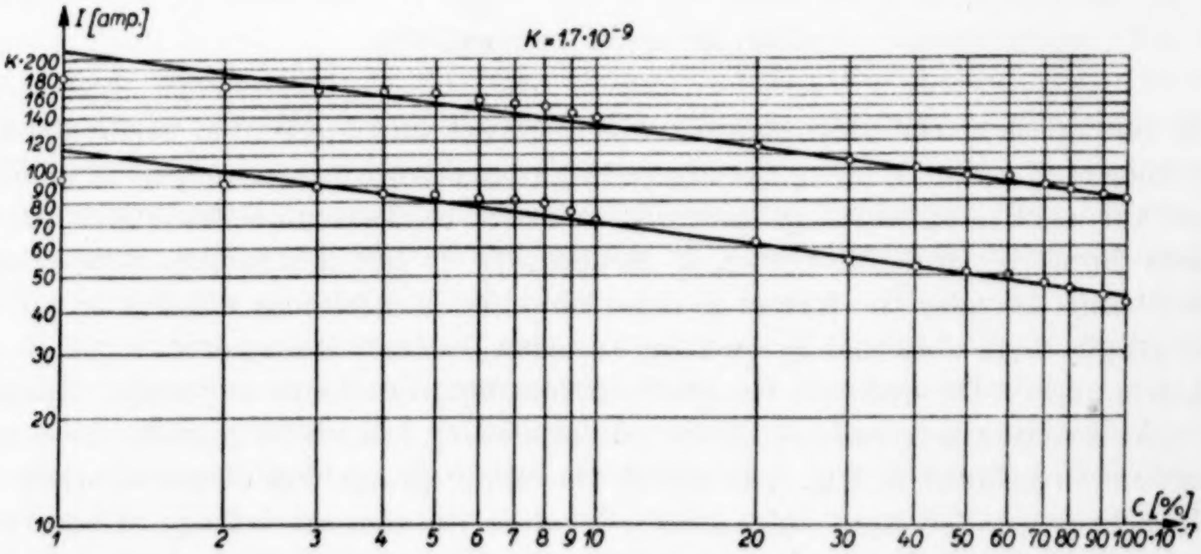

Fig. 4. The intensity of coloration of the same series of little discs of silica gel in dependence upon the initial concentration of methylene blue, plotted on log-log graph paper

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of dealing with identical coloration intensities and the same light source. We explain this effect by the change of the light flux as well as by the change of the light spectrum, which, for lower potential differences, is shifted towards greater wavelengths. This fact completely justifies the connection diagram of the apparatus with which we worked.

In Fig. 4 the magnitudes from the previous figure are shown, only this time in log-log coordinates. As a nearly straight line is obtained we come to the conclusion that the dependence of the variables stated is a logarithmic one.

In Fig. 5 this dependence, according to a long series of tests, is shown in a

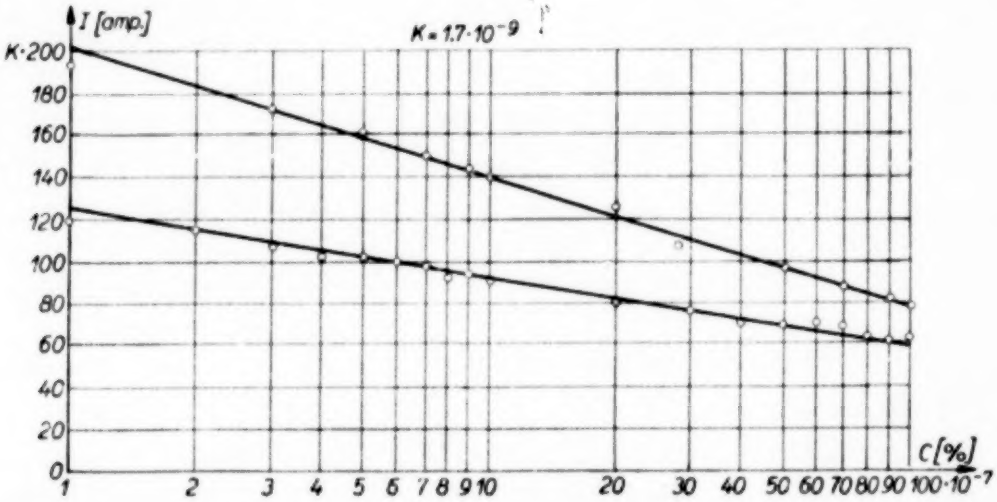

Fig. 5. The intensity of coloration of two series of little discs of silica gel in dependence upon the initial concentration of methylene blue, plotted on semilogarithmic graph paper.

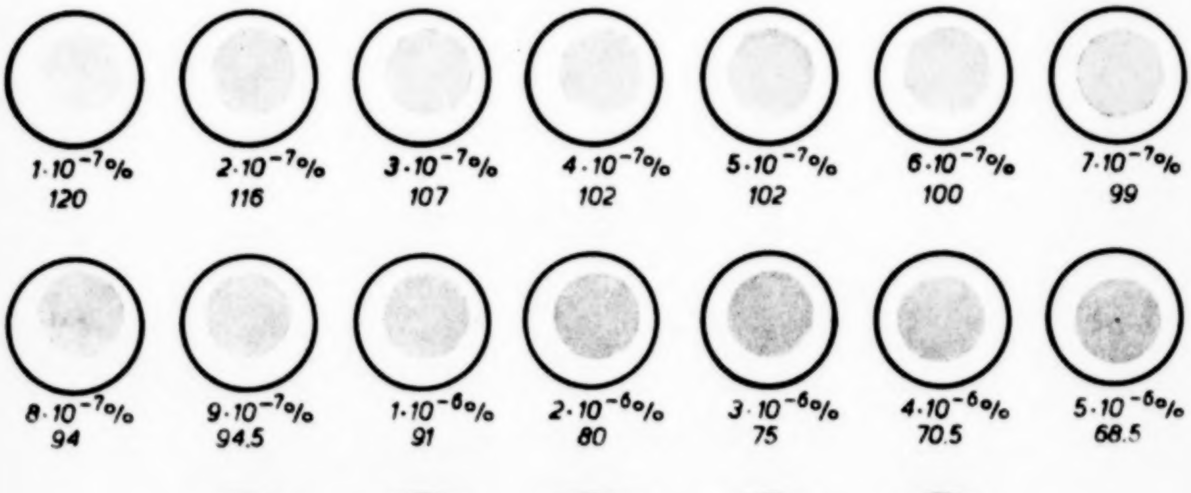
$1\cdot10^{-7}$%
120
$2\cdot10^{-7}$%
116
$3\cdot10^{-7}$%
107
$4\cdot10^{-7}$%
102
$5\cdot10^{-7}$%
102
$6\cdot10^{-7}$%
100
$7\cdot10^{-7}$%
99
$8\cdot10^{-7}$%
94
$9\cdot10^{-7}$%
94.5
$1\cdot10^{-6}$%
91
$2\cdot10^{-6}$%
80
$3\cdot10^{-6}$%
75
$4\cdot10^{-6}$%
70.5
$5\cdot10^{-6}$%
68.5
$6\cdot10^{-6}$%
70.0
$7\cdot10^{-6}$%
64.5
$8\cdot10^{-6}$%
62.0
$9\cdot10^{-6}$%
60.0
$1\cdot10^{-5}$%
61

Fig. 6. A series of little discs of silica gel with methylene blue adsorbed on them.

semilogarithmic system. The upper graph represents the results of measurement with a voltage of 6 V while the lower graph represents the measurement results of the samples (Fig. 6) enclosed in this paper, in which the light source of the colorimeter was supplied with a voltage of 5.5 V.

One of the disadvantages of the adsorbent coloured surfaces, at the beginning of our work, was a certain coloration non-homogeneity. In order to lessen it we performed a series of tests adding capillary active materials to the solution with the intention of increasing the wetting ability of the surface of the adsorbent. In this we used $0.1N$ NaOH, $0.1N$ Na_2CO_3 as well as ethyl- and butyl-alcohol. These liquids were added in amounts of 2 to 100 ml of solution at a time. Alkaline solutions give a very good surface coloration homogeneity but the coloration intensity is lower than that obtained from a neutral water solution. The coloration shade is somewhat more greenish, which we consider to come from an increased amount of copper salts arising from the brass. When working with butyl alcohol we could not observe any greater effect on the homogeneity of coloration, whereas with ethyl alcohol we had good results which we interpret, on one hand, by an increased wettability, and on the other, by a probable solution of nitrocellulose lacquer binding together the adsorbent particles which enables a more intimate contact with the adsorbent itself. It is obvious that great care should be taken in choosing the capillary active substances for they can have either physical or chemical effects on the dissolved coloured material.

In a series of tests we studied the effect of pH on adsorption. In order to avoid any considerable effect on the dispersion of the coloured material dissolved and of any chemical effect, we worked in the range of pH from 6 to 8. We obtained the desired pH by the use of buffer solutions according to CLARK AND LUBS[9], considering that extremely small quantities of methylene blue could not change, to a great extent, the pH of the buffers prepared in this way.

The measurement results we obtained are given in Table I:

TABLE I

Concentration %	pH		
	6	7	8
	Galvanometer deflection		
0.000002	135	—	137
0.000003	—	128	—
0.000004	118	118	118
0.000005	115	114.5	114
0.000006	—	109.2	111
0.000007	105.5	106	106
0.000008	—	105.5	105

It may be seen from the table that in the range stated above the effect of pH under our working conditions is negligible, as it is less than the error limit of the method.

The coloured surfaces are homogeneous and the colour has a somewhat more greenish shade. In the logarithmic coordinate system the stated points lie on a straight line.

We tried to determine concentrations of Congo red in aqueous solutions by the same process. As the operation was carried out with an acid adsorbent and acid coloured material, the surface of the adsorbent, owing to a poor adsorption, was faintly coloured. We therefore turned to chromatographic aluminium trioxide with reactivity of which we counted owing to its amphoteric character. In this case aluminium oxide proved better. We noticed that in either case the filter paper was much more intensively coloured than the corresponding adsorbent. We were induced by this to use only filter paper as an adsorbent for this adsorption. To strengthen the filter paper mechanically and at the same time to diminish the rate of flow of the solution, on one of its sides we sprayed cellulose nitrate solution of the same concentration as in the previous cases. During the adsorption the unsprayed side of the filter paper was turned down. The results of measurements of the coloured surfaces thus obtained are shown in Fig. 7.

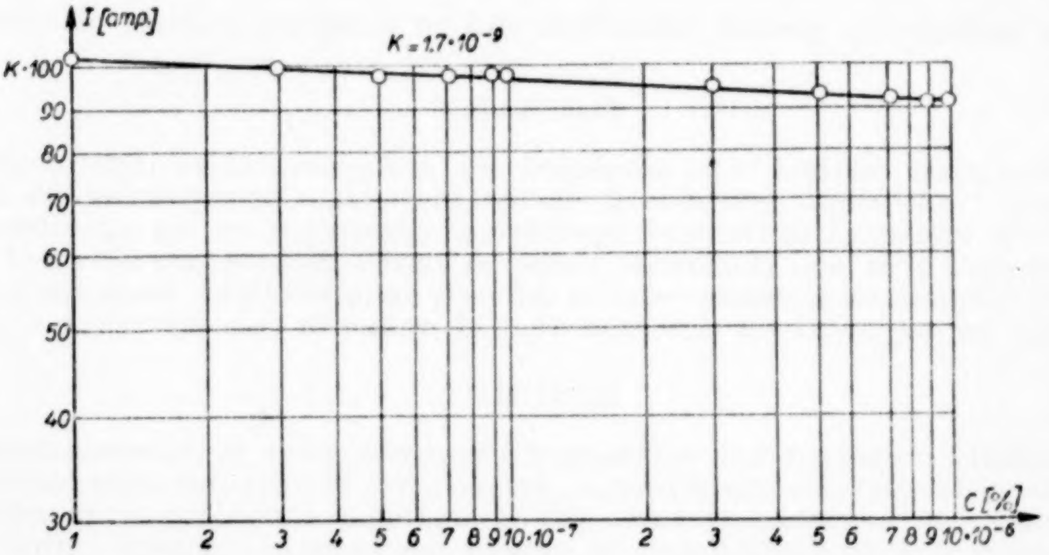

Fig. 7. The intensity of coloration of filter paper discs in dependence upon the initial concentration of Congo red plotted on log-log graph paper

It may be seen from the graph that the difference in photo currents, for the same concentrations, are considerably smaller for Congo red than for methylene blue. This comes in the first place from the fact that the sensitivity of the selenium element is less for the red than for the blue part of the spectrum.

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CONCLUSIONS

Although the ultimate result of determination of the suggested adsorption method is a compromise between several adsorption equilibria: on adsorbent, on filter paper, on the walls of the vessels and apparatus, still this method may successfully be used for semi-quantitative measurements of extremely dilute coloured solutions, because in the end the establishment of adsorption equilibria with all surfaces with which the solution comes into contact during the reaction is reached. As the quantity of coloured materials adsorbed under the equivalent conditions is a function of the concentration only, the unknown value may be determined on the basis of previous graduations with known concentrations. This is considerably facilitated by the fact that the graphically illustrated dependence: the initial concentration — photo-current obtained by colorimetric measurements of the surface of the adsorbent in log-log or semilogarithmic system, is a straight line. This method requires a greater volume of the solution the concentration of which is being determined. The reproducibility is satisfactory.

If the basic characteristic of this method is adsorption — a common phenomenon in nature — this method provides possibilities for the determination of extremely low concentrations not only of coloured — but also of colourless materials, providing these are made visible on the adsorbent either by chemical reactions or by some physical or physicochemical processes. It is only necessary to find a sufficiently specific adsorbent and an adequate inducer of coloration.

SUMMARY

An adsorption method was developed for semiquantitative determination of very dilute, "colourless" solutions of coloured materials. Concentrating the coloured material by means of isothermal equilibrium adsorption on an adsorbent of a limited surface area and thickness, visibly coloured surfaces are obtained which, by direct colorimetric measurements in diffusely reflected light, using the reference curve, can be employed for determination of unknown concentrations.

RÉSUMÉ

Les auteurs proposent une méthode d'adsorption pour la détermination semi-quantitative de solutions très diluées - ,,non-colorées" - des substances colorées. Par concentration de la substance colorée, par adsorption isothermique sur un adsorbant, de surface et d'épaisseur limitées, on obtient des surfaces colorées, permettant la détermination colorimétrique des concentrations inconnues, par comparaison avec une courbe étalon.

ZUSAMMENFASSUNG

Es ist eine Adsorptions-Methode zur halbquantitativen Bestimmung sehr verdünnter — ,,farbloser" — Lösungen von Farbstoffen ausgearbeitet worden. Durch Anreicherung des Farbstoffes mittels isothermer Gleichgewichts-Adsorption an einem Adsorbens, begrenzter Oberfläche und Dicke, erhält man sichtlich gefärbte Flächen, die durch direktes Kolorimetrieren im diffus-reflektierten Licht ausgewertet und auf Grund einer Eichkurve zur Bestimmung der unbekannten Konzentration dienen können.

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THEORETICAL TREATMENT OF THE SPECTROPHOTOMETRIC TITRATION OF BIVALENT CATIONS WITH COMPLEXON-III AND METAL-SPECIFIC INDICATORS

by

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INTRODUCTION

Metal-specific indicators have been used, *inter alia*, in the titration of Ca and Mg with complexon-III solution, where murexide and eriochrome black T respectively act as indicators (SCHWARZENBACH c.s.).

When, in order to define our thoughts, we take the Ca-titration as an example, the important point is that the Ca-murexide compound exhibits in alkaline medium a different colour (red) from the free murexide (blue violet), so that beyond the equivalence point hardly any colour change takes place. The use of murexide as indicator is not identical with the employment of two-colour indicators in acid-base and redox titrations.

This type of colour change is more difficult to detect, even after some practice, and for this reason we have tried to determine the equivalence point by spectrophotometric means. By spectrophotometric titration we understand the production of the curve: Extinction as a function of the amount of titer solution added, and the derivation of the equivalence point from this curve.

Before proceeding to the practical application (see our next publication) it seemed of interest to us first to look at the theoretical course of this titration to find out whether a sharp equivalence point was indeed to be expected, and to ascertain what would be the optimum conditions for the success of the titration.

THEORETICAL DISCUSSION

List of principal symbols used

m = [M]: concentration of the metal ions
c = [C]: concentration of the metal-free titer substance
i = [I]: concentration of the metal-free indicator
c' = [MC]: concentration of the metal-containing titer substance
i' = [MI]: concentration of the metal-containing indicator
m_t = total metal ion concentration

c_t = total concentration of the titer substance
i_t = total concentration of the indicator
E_t = total extinction of the solution to be titrated
ε = molar extinction coefficient of the metal-free indicator
ε' = molar extinction coefficient of the metal-containing indicator
l = length of the light path through the solution to be titrated
v = titer solution added, in ml
v_0 = volume of the metal ion solution to be titrated, in ml
$\mu = \dfrac{c_t}{m_t}$: relative concentration of the titer substance
$K_c = \dfrac{c'}{m.c}$: stability constant of MC
$K_I = \dfrac{i'}{m.i}$: stability constant of MI
$a = \dfrac{i}{i_t}$: ratio of $\dfrac{[I]}{[MI]+[I]}$
$h = [H^+]$: hydrogen ion concentration of the solution to be titrated
n = molarity of the titer solution
H_5I = formula of the indicator
$^*i = i_1 + i_2 + i_3$: sum of the concentrations of the metal-free indicator components; $i_1 = [H_4I^-]$, $i_2 = [H_3I^{-2}]$, $i_3 = [H_2I^{-3}]$
$K_2 = \dfrac{h.i_2}{i_1}$: dissociation constant of H_4I^-
$K_3 = \dfrac{h.i_3}{i_2}$: dissociation constant of H_3I^{-2}
$^*i' = i_1' + i_2' + i_3'$: sum of the concentrations of the metal-containing indicator components
$i_1' = [MH_4I^+]$, $i_2' = [MH_3I]$, $i_3' = [MH_2I^-]$
$K_2' = \dfrac{h.i_2'}{i_1'}$: dissociation constant of MH_4I^+
$K_3' = \dfrac{h.i_3'}{i_2'}$: dissociation constant of MH_3I
H_2Y^{-2} = formula of the complex-forming ion in the titer substance
$^*c = c_1 + c_2 + c_3$: sum of the concentrations of the metal-free titer substance components
$c_1 = [H_2Y^{-2}]$, $c_2 = [HY^{-3}]$, $c_3 = [Y^{-4}]$
$k_3 = \dfrac{h.c_2}{c_1}$: dissociation constant of H_2Y^{-2}

$k_4 = \frac{h.c_3}{c_2}$: dissociation constant of HY^{-3}

$*c' = c_1' + c_2'$: sum of the concentrations of the metal-containing titer substance components

$c_1' = [MHY^-]$, $c_2' = [MY^{-2}]$

$k_1' = \frac{c_1'}{m.c_2}$: stability constant of MHY^-

$k_2' = \frac{c_2'}{m.c_3}$: stability constant of MY^{-2}

$*K_I = \frac{*i'}{m.*i}$: complex-forming capacity of the indicator

$K'_I = \frac{i_1'}{m.i_1}$: stability constant of MH_4I^+

$*K_c = \frac{*c'}{m.*c}$: complex-forming capacity of the titer substance

(Symbols with superscript ′ are related to metal-containing substances)

I. *Derivation of a general expression for a spectrophotometric titration curve*

For simplicity's sake we will start by assuming that the complex-forming titer substance as well as the indicator and their respective metals compounds occur each in only one form, so that any further dissociations of the kinds of ions here referred to are left out of account in this chapter (for a derivation of the actual position reference is made to Chapter IV).

How does the extinction change during the titration?

During the titration there are present in the solution: metal ions M, anions C, which are capable of binding the metal ions in MC complexes, and indicator ions I, which can also form MI complexes with the metal ions. We therefore have the following equilibria: $M + C \rightleftharpoons MC$ (constant: K_c)

$M + I \rightleftharpoons MI$ (constant: K_I)

The effect of the two coloured compounds (I and MI) on the total extinction of the solution can now be formulated as follows:

$$\begin{aligned} E_t &= \varepsilon . l . i + \varepsilon' . l . i' \\ &= \varepsilon . l . a . i_t + \varepsilon' . l . (1—a) . i_t \\ &= \varepsilon' . l . i_t + (\varepsilon—\varepsilon') . l . a . i_t \end{aligned}$$

If we now write $E_t — \varepsilon' . l . i_t = E$, then:

$$E = (\varepsilon — \varepsilon') . l . a . i_t \qquad (1)$$

(through this expedient it seems as if only I is coloured)

E is therefore proportional to $a . i_t$ ($= i$)

We are, however, looking for: $E = E(v)$; now i is related to c_t, and c_t in turn is proportional to v, so that if $i = i(c_t)$ is known, $E = E(v)$ can easily be derived from this.

Derivation of the function: $i = i(c_t)$

From K_c and K_I it follows that:
$$c' = K_c \,.\, m \,.\, c \tag{2}$$
$$i' = K_\mathrm{I} \,.\, m \,.\, i \tag{3}$$

Substitution of (2) and (3) in
$$m_t = m + c' + i' \tag{4}$$
$$c_t = c + c' \tag{5}$$
$$i_t = i + i' \tag{6}$$

gives:
$$m_t = m + K_c \,.\, m \,.\, c + K_\mathrm{I} \,.\, m \,.\, i \tag{7}$$
$$c_t = c + K_c \,.\, m \,.\, c \tag{8}$$
$$i_t = i + K_\mathrm{I} \,.\, m \,.\, i \tag{9}$$

From (9) it follows that:
$$m = \frac{i_t - i}{i \,.\, K_\mathrm{I}} \tag{10}$$

From (8) it follows that:
$$c = \frac{c_t}{1 + K_c \,.\, m} \tag{11}$$

Substitution of (10) in (11) gives:
$$c = \frac{c_t}{1 + K_c \,.\, \dfrac{i_t - i}{i \,.\, K_\mathrm{I}}} \tag{12}$$

From (10), (12), and (7) it follows that:
$$\begin{aligned} c_t &= \left(\frac{1}{K_c} + \frac{i_t - i}{i \,.\, K_\mathrm{I}}\right) \cdot \left\{ \frac{m_t \,.\, i \,.\, K_\mathrm{I}}{i_t - i} - (1 + i \,.\, K_\mathrm{I}) \right\} \\ &= m_t - (i_t - i) \,.\, \left(1 + \frac{1}{i \,.\, K_\mathrm{I}}\right) + i \,.\, \frac{K_\mathrm{I}}{K_c} \cdot \left\{ \frac{m_t}{i_t - i} - \left(1 + \frac{1}{i \,.\, K_\mathrm{I}}\right) \right\} \end{aligned} \tag{13}$$

When we disregard the dilution occuring during the titration we may consider m_t and i_t also as constants.

We have now derived c_t as a function of the third degree of i, and c_t can therefore be easily shown in a graph. From this we can then read the desired relationship of i (and consequently also of E) as a function of the amount of titer substance added.

What are the boundaries between which i varies during the titration?

At the beginning of the titration there is only the indicator equilibrium: $\mathrm{M} + \mathrm{I} \rightleftarrows \mathrm{MI}$

From $i_t = i + i'$, $m_t = m + i'$, and $K_\mathrm{I} = \dfrac{i'}{m \,.\, i}$ it follows that:
$$K_\mathrm{I} \,.\, i^2 + i \,.\, (1 + K_\mathrm{I} \,.\, m_t - K_\mathrm{I} \,.\, i_t) - i_t = 0 \tag{14}$$

Since only positive values of i are realizable, we have:

$$i = \frac{m_t - i_t + \frac{1}{K_I}}{2}\left[-1 + \sqrt{\left\{1 + \frac{4\, i_t}{K_I\,.\,(m_t - i_t + \frac{1}{K_I})^2}\right\}}\right] \qquad (15)$$

In general we have:

$$\frac{4\, i_t}{K_I\,.\,(m_t - i_t + \frac{1}{K_I})^2} \ll 1 \ (e.g.\ i_t = 10^{-5},\ m_t = 10^{-2}, K_I = 10^5)$$

If $\Delta \ll 1$, we may write $\sqrt{1 + \Delta}$ as $\approx (1 + \frac{1}{2}\Delta)$, and then we have $-1 + \sqrt{1 + \Delta} \approx \frac{1}{2}\Delta$, so that (15) can be reduced to:

$i = \dfrac{i_t}{K_I\,(m_t - i_t + \frac{1}{K_I})}$ (16), which therefore denotes the initial value for i.

The maximum value that i may assume is i_t, so that the boundaries between which i varies during the titration may be stated as follows:

$$\frac{i_t}{1 + K_I\,.\,(m_t - i_t)} < i < i_t \qquad (17)$$

Transformation of $c_t = c_t(i)$ *into* $\mu = \mu\,(\alpha)$

The curves $c_t = c_t\,(i)$ to be expected under different conditions, expressed by the equation (13), may be made graphically comparable most satisfactorily if we change (13) in such a way that the absolute values of the concentrations c_t and i are replaced by the relative values $\mu\,(= \frac{c_t}{m_t})$ and $\alpha\,(= \frac{i}{i_t})$ (μ passes from 0, at the beginning of the titration, to 1 at the equivalence point; if the conditions are well chosen, α should be approximately 1 at the equivalence point).

$$\mu = 1 - \frac{1}{m_t}.\,(1-\alpha).\,(i_t + \frac{1}{\alpha.K_I}) + \alpha.\,\frac{K_I}{K_c}.\left\{\frac{1}{1-\alpha} - \frac{1}{m_t}.\,(i_t + \frac{1}{\alpha.K_I})\right\} \qquad (18)$$

If we now call: $-\dfrac{1}{m_t}\,(1 - \alpha)\,.\,(i_t + \dfrac{1}{\alpha.K_I}) = t_i$ (19)

and $\alpha\,.\,\dfrac{K_I}{K_c}.\left\{\dfrac{1}{1-\alpha} - \dfrac{1}{m_t}.\,(i_t + \dfrac{1}{\alpha.K_I})\right\} = t_m$ (20)

then $\mu = 1 + t_i + t_m$ (21)

From (17) it follows that the boundaries between which α may vary are:

$$\frac{1}{1 + K_I\,.\,(m_t - i_t)} < \alpha < 1 \qquad (22)$$

For what values of α are we justified in disregarding the term t_m in relation to $(1 + t_i)$?

From (20) it follows that:

$$i_t \cdot (1-\alpha)^2 - (1-\alpha) \cdot \left(m_t + i_t + \frac{1}{K_I} + m_t \cdot \frac{K_c}{K_I} \cdot t_m\right) + m_t = 0 \qquad (23)$$

If we now write: $m_t + i_t + \dfrac{1}{K_I} + m_t \cdot \dfrac{K_c}{K_I} \cdot t_m = \beta$ (24)

then: $i_t \cdot (1-\alpha)^2 - \beta \cdot (1-\alpha) + m_t = 0$ (25)

In view of the fact that $0 < \alpha < 1$, we have:

$$(1-\alpha) = \frac{\beta - \sqrt{(\beta^2 - 4\, m_t \cdot i_t)}}{2\, i_t}$$

$$= \frac{\beta}{2\, i_t} \cdot \left\{1 - \sqrt{\left(1 - \frac{4\, m_t \cdot i_t}{\beta^2}\right)}\right\} \qquad (26)$$

In general, $\beta^2 \gg 4\, m_t \cdot i_t$ (this is easily seen when we square (24), which gives: $\beta^2 = m_t{}^2 + 2\, m_t \cdot i_t + i_t{}^2 + \ldots\ldots\ldots$

$$= 4\, m_t \cdot i_t \left(\tfrac{1}{2} + \frac{m_t}{4\, i_t} + \frac{i_t}{4 m_t}\right) + \ldots\ldots\ldots$$

Now $m_t \gg i_t$, so that $\beta^2 \gg 4\, m_t \cdot i_t$)

Since for $\triangle \ll 1$ we have: $1 - \sqrt{1 - \triangle} \approx \frac{1}{2}\triangle$, we may write (26) as:

$$(1-\alpha) = \frac{m_t}{\beta} \qquad (27)$$

If we now substitute (24) in (27), we obtain:

$$\alpha = 1 - \frac{1}{1 + \dfrac{K_c}{K_I} \cdot t_m + \dfrac{1}{m_t} \cdot \left(i_t + \dfrac{1}{K_I}\right)} \qquad (28)$$

From (20) and (28) it is evident that when K_I, K_c, i_t, and m_t are fixed, every t_m is associated with a definite value for α while t_m and α also move in the same direction.

If we now wish to calculate μ with an accuracy of, say, 0.001, t_m may be disregarded, if $t_m \leq 0.001$, and the corresponding α can be derived.

In those cases where we calculate μ with an accuracy of t_m, we have:

$$\mu = 1 + t_i = 1 - \frac{1}{m_t} \cdot (1-\alpha) \cdot \left(i_t + \frac{1}{\alpha \cdot K_I}\right) \qquad (29)$$

and this is admissible, if:

$$\frac{1}{1 + K_I \cdot (m_t - i_t)} < \alpha < \left\{1 - \frac{1}{1 + \dfrac{K_c}{K_I} \cdot t_m + \dfrac{1}{m_t} \cdot \left(i_t + \dfrac{1}{K_I}\right)}\right\} \qquad (30)$$

It now appears that a very large part of the line $\mu = \mu(\alpha)$ can be calculated with a reasonable degree of accuracy, even if t_m is disregarded.

From the curve $\mu = \mu(\alpha)$ we can again read: $\alpha = \mu(\alpha)$.

II. *The form of the curve $a = a(\mu)$ and the effect of the different magnitudes on the form*

In order to gain a picture of the course of a curve represented by equation (18), the following numerical values were introduced into this expression, upon which the accompanying graph (Fig. 1) was obtained.

curve	m_t	i_t	K_{I}	K_c
A_1	$\frac{1}{3}.10^{-2}$(g.mol./l)	3.10^{-4}(g.mol./l)	$\frac{1}{8}.10^{6}$	4.10^{10}

The striking feature of this curve is the characteristic "break" at the equivalence point; as will be apparent from the following, this phenomenon always occurs when $K_c \gg K_{\text{I}}$.

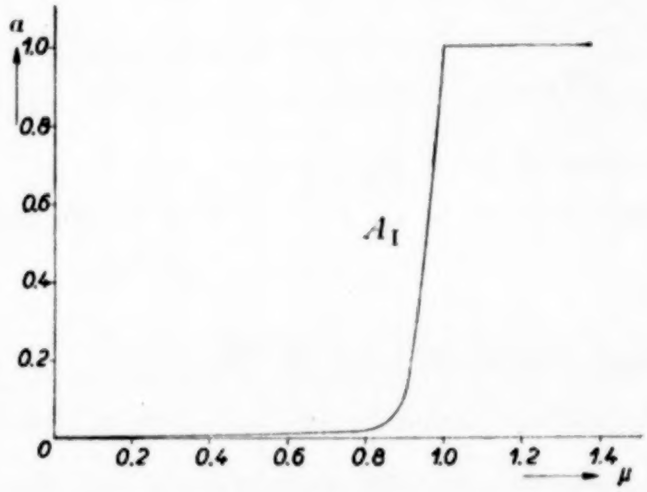

Fig. 1. $a = a(\mu)$ (for $m_t = \frac{1}{3}.10^{-2}$, $i_t = 3.10^{-4}$, $K_{\text{I}} = \frac{1}{8}.10^{6}$, $K_c = 4.10^{10}$)
The fraction of liberated indicator (murexide) as a function of the fraction of theoretically required titer substance (complexon-III).

If $K_c \gg K_{\text{I}}$, we may apply the approximation expression (29) from the beginning of the titration to close upon the equivalence point; for the present we will therefore examine the effect of i_t, K_{I}, and m_t on the curve when $K_c \gg K_{\text{I}}$.

The effect of the indicator concentration i_t

Fig. 2 comprises the curves, A_1 — A_3, obtained by substitution of the given values in the equations concerned.

The graph shows that at a lower indicator concentration the range of the colour change is narrowed, and the curve in that range has a steeper slope (the mathematical limit for $i_t = 0$ is represented by curve A_4).

The absolute value of the extinction, however, is lowered by the use of a low indicator concentration. We can, however, raise the extinction by increasing

$(\varepsilon - \varepsilon')$ and l, respectively. The sharpest colour change may therefore be expected at a wavelength with a maximum extinction difference between the two coloured components of the indicator (I and MI), because there the concentration of the indicator may be at its lowest.

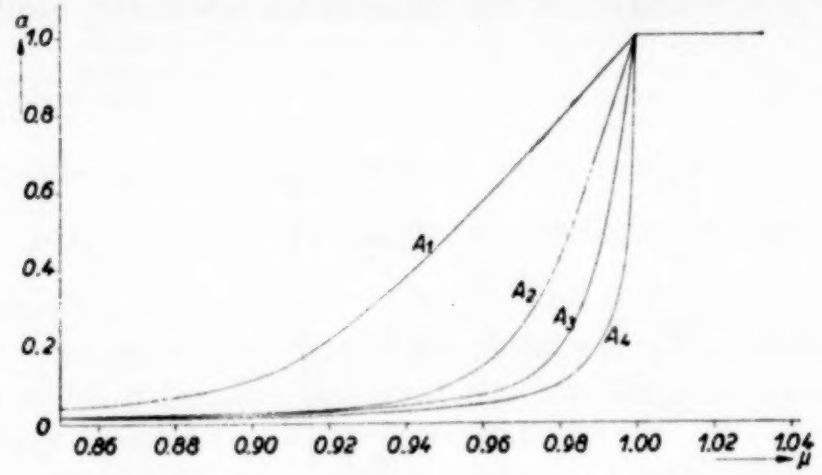

Fig. 2. Effect of the indicator concentration (abscissa on an enlarged scale).

TABLE I

curve	m_t	i_t	K_I	K_c
A_1	$\frac{1}{3}\cdot 10^{-2}$	$3\cdot 10^{-4}$	$\frac{1}{8}\cdot 10^{6}$	$4\cdot 10^{12}$
A_2	,,	$1\cdot 10^{-4}$	,,	,,
A_3	,,	$0{,}4\cdot 10^{-4}$	,,	,,

The effect of the value of the stability constant K_I

From $\mu = 1 + t_i$

$$= \left(1 - \frac{(1-\alpha).i_t}{m_t}\right) - \left(\frac{1-\alpha}{\alpha.m_t}\right)\cdot\frac{1}{K_I} \tag{31}$$

it follows that μ is linearly dependent on $\frac{1}{K_I}$ (provided $K_c \gg K_I$) at a definite value of α.

When $K_I \rightarrow \infty$, then $\frac{1}{K_I} \rightarrow 0$, and the equation (31) then passes into:

$$\mu = 1 - \frac{(1-\alpha).i_t}{m_t}$$

$$= (1 - \frac{i_t}{m_t}) + \frac{i_t}{m_t}.\alpha \tag{32}$$

In the limiting case we get curve B_4 (Fig. 3); the slope of the rising part of this curve is $\frac{m_t}{i_t}$.

A quantitative picture of the course of the curves for different values of K_I is provided by Fig. 3. (Note: the high initial value of curve B_1 is to be ascribed to a considerable dissociation of the MI complex before the addition of the titer substance.)

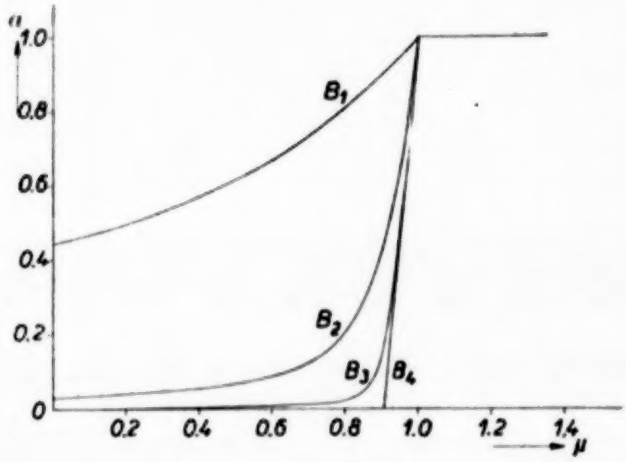

Fig. 3. Effect of the stability constant K_I of the indicator.

TABLE II

curve	m_t	i_t	K_I	K_c
B_1	$\frac{1}{3}\cdot 10^{-2}$	$3\cdot 10^{-4}$	$4\cdot 10^{2}$	$4\cdot 10^{12}$
B_2	,,	,,	$1\cdot 10^{4}$	,,
B_3	,,	,,	$\frac{1}{8}\cdot 10^{6}$	,,

The effect of the total metal ion concentration m_t

From $$\mu = 1 - (1-\alpha) \cdot (i_t + \frac{1}{\alpha . K_I}) \cdot \frac{1}{m_t} \qquad (29)$$

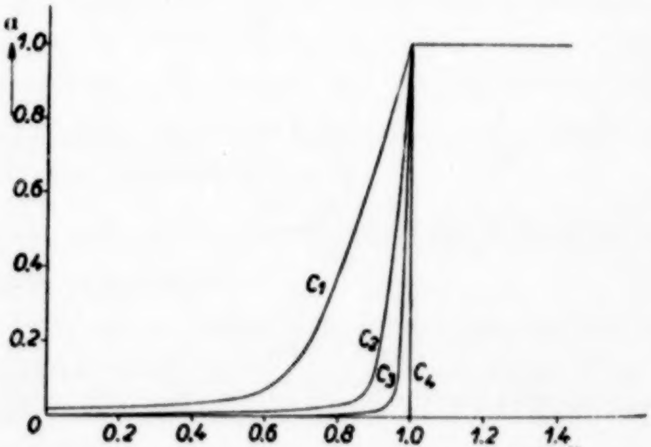

Fig. 4. Effect of the concentration of the substance to be determined.

TABLE III

curve	m_t	i_t	K_I	K_c
C_1	$0.1 \cdot 10^{-2}$	$3 \cdot 10^{-4}$	$\frac{1}{8} \cdot 10^{6}$	$4 \cdot 10^{12}$
C_2	$\frac{1}{3} \cdot 10^{-2}$	,,	,,	,,
C_3	$1 \cdot 10^{-2}$	,,	,,	,,

it follows that there exists an approximate linear relationship between μ and $\frac{1}{m_t}$ (provided $K_c \gg K_I$), if the other magnitudes are kept constant.

$$\lim_{m_t \to \infty} \mu = 1 \qquad (33)$$

(vide Fig. 4, curve C_4).

A quantitative picture of the effect of the metal ion concentration is furnished by Fig. 4, from which it becomes apparent that the titration becomes more accurate if m_t is high, just as in all titration methods.

The effect of the value of the stability constant K_c

Up to this point we have always assumed that $K_c \gg K_I$, in order to be able to calculate with the approximation equation (29) even when the values of $(1-\alpha)$ are very low. It always appeared as if a sharp break occurred at $\mu = 1$. If, however, the stability constant K_c becomes of the same order of magnitude as K_I, this break will disappear.

Figs. 5 and 6 furnish a quantitative picture of this, obtained by substitution

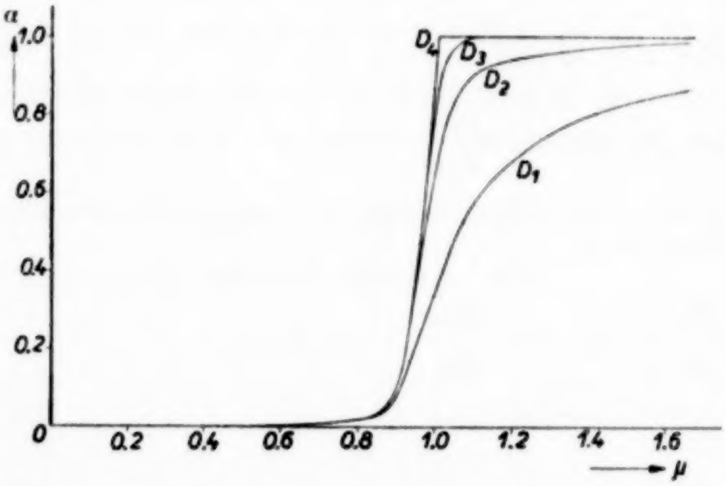

Fig. 5. Effect of the stability constant K_c of the titer substance.

TABLE IV

curve	m_t	i_t	K_I	K_c	$\log K_c/K_I$
D_1	$\frac{1}{3} \cdot 10^{-2}$	$3 \cdot 10^{-4}$	$\frac{1}{8} \cdot 10^{6}$	$\frac{1}{8} \cdot 10^{7}$	1
D_2	,,	,,	,,	$\frac{1}{8} \cdot 10^{8}$	2
D_3	,,	,,	,,	$\frac{1}{8} \cdot 10^{9}$	3
D_4	,,	,,	,,	$\frac{1}{8} \cdot 10^{13}$	7

of the given numerical values in the equations concerned. The lines for which $\log \frac{K_c}{K_\text{I}} > 5$ practically coincide.

We may conclude from this that according as K_c approaches the same order of magnitude as K_I, the familiar "break" disappears and that an accurate determination of the equivalence point, such as was hitherto within the range of possibility, is scarcely possible any longer. With curve D_3 the approximate equivalence point can still be found through extrapolation, but with D_2 and D_1 this will produce altogether faulty results.

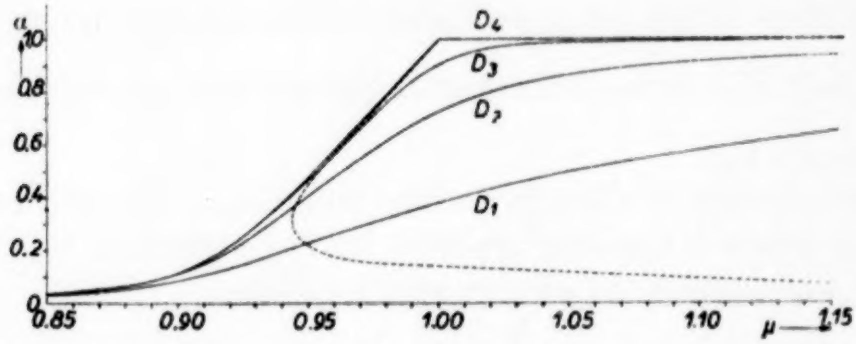

Fig. 6. Effect of the stability constant K_c of the titer substance (abscissa on an enlarged scale).
------------ = locus of the points of inflexion (the points of inflexion do not coincide with the equivalence points!).

The slope of the curve $\alpha = \alpha\ (\mu)$

For this we have to derive $\frac{d\alpha}{d\mu}$

From (21) it follows that: $\frac{d\mu}{d\alpha} = \frac{dt_i}{d\alpha} + \frac{dt_m}{d\alpha}$

If we now call: $\frac{dt_i}{d\alpha} = t_i'$ and $\frac{dt_m}{d\alpha} = t_m'$, then:

$$\frac{d\mu}{d\alpha} = t_i' + t_m' \tag{34}$$

and
$$\frac{d\alpha}{d\mu} = \frac{1}{t_i' + t_m'} \tag{35}$$

From (19) it follows that:

$$t_i' = -\frac{1}{m_t} \cdot \left\{ (1-\alpha) \cdot \left(\frac{-1}{\alpha^2.K_\text{I}}\right) - \left(i_t + \frac{1}{\alpha.K_\text{I}}\right) \right\}$$

$$= \frac{1}{m_t} \cdot \left(i_t + \frac{1}{\alpha^2.K_\text{I}}\right) \tag{36}$$

From (20) it follows that: $t_m' = \frac{K_I}{K_c}\cdot\left\{\frac{1}{(1-\alpha)^2} - \frac{i_t}{m_t}\right\}$ (37)

Substitution of (36) and (37) in (35) gives:

$$\frac{d\alpha}{d\mu} = \frac{m_t}{i_t + \frac{1}{\alpha^2.K_I} + \frac{K_I}{K_c}.\left\{\frac{m_t}{(1-\alpha)^2} - i_t\right\}} \quad (38) \quad \text{(vide Fig. 7)}$$

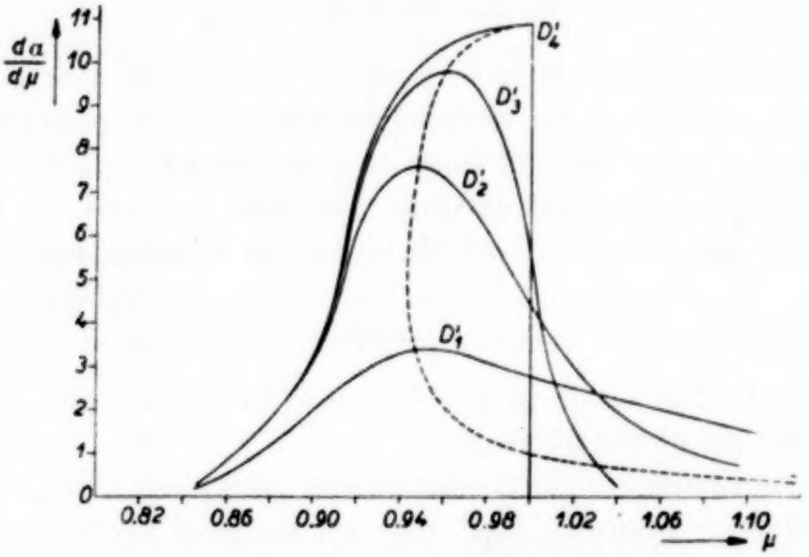

Fig. 7. The derived curve at different values of K_c.
-------------- = locus of the maxima.

III. Transformation of the curve $\alpha = \alpha(\mu)$ into $E = E(v)$

In order to ascertain what curves we shall find in practice, where we always determine E as a function of v, the data of the curves A_2 and A_3 (Fig. 2) were transformed with the aid of equation (1) and the expression for $\mu = \frac{c_t}{m_t} = \frac{n.v}{v_o}\cdot\frac{1}{m_t}$, which resulted in the curves A_2' and A_3' (Fig. 8).

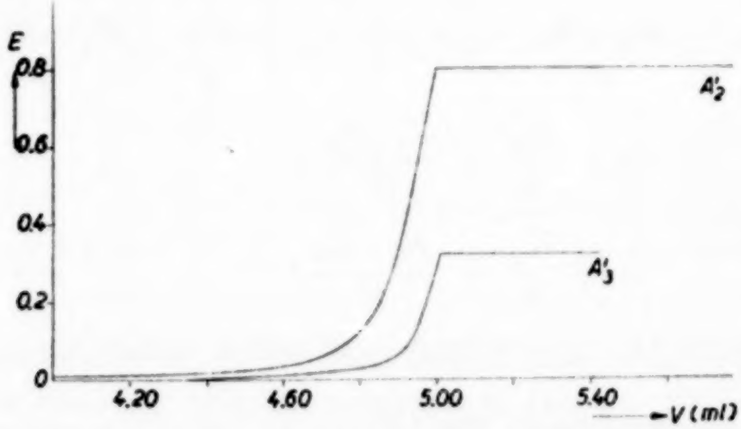

Fig. 8. The extinction change as a function of the volume of titer substance added.

Use was made of the numerical values from the following table:

curve	m_t	i_t	K_I	K_c	$(\varepsilon - \varepsilon').l$	n	v_0
A_2'	$\frac{1}{3}\cdot 10^{-2}$	$1\cdot 10^{-4}$	$\frac{1}{8}\cdot 10^{6}$	$4\cdot 10^{12}$	$0.8\cdot 10^{4}$	0.1	150 ml
A_3'	,,	$0.4\cdot 10^{-4}$	,,	,,	,,	,,	,,

IV. The effect of the acidity on the titration

In the above we have, in order to avoid complication, disregarded the effect of the pH of the solution to be titrated on the stability constants K_I and K_c.

For completeness' sake we still have to consider this effect; the K_I and K_c appearing in the preceding calculations are now replaced by the magnitudes $^*K_I$ and $^*K_c$, the dependence of which on the pH is examined below.

The effect of the pH on the complex-forming capacity of the indicator $^*K_I$

Usually the indicator anion is capable of splitting off one or more protons, dependent on the pH of the solution.

Thinking of murexide (= acid ammonium purpurate: $NH_4H_4C_8O_6N_5$), we represent the indicator anion by H_4I^- (the 1st stage of purpuric acid is strong!). With a bivalent metal ion M^{+2} this anion will be able to form a complex as follows:

$M^{+2} + H_4I^- \rightleftharpoons MH_4I^+$ (stability constant K'_I)

If we further assume that H_4I^- and MH_4I^+ are both capable of splitting off two protons in the pH range under consideration, we have the following equilibria:

$$H_4I^- \rightleftharpoons H^+ + H_3I^{-2}$$

$$H_3I^{-2} \rightleftharpoons H^+ + H_2I^{-3}$$

$$MH_4I^+ \rightleftharpoons H^+ + MH_3I$$

$$MH_3I \rightleftharpoons H^+ + MH_2I^-$$

Making use of the notations for $^*i$, $^*i'$, K_2, K_3, K_2', K_3', and $^*K_I$, this leads to:

$$^*i = i_1 . \left(1 + \frac{K_2}{h} + \frac{K_2 \,.\, K_3}{h^2}\right),\ ^*i' = i_1' . \left(1 + \frac{K_2'}{h} + \frac{K_2' \,.\, K_3'}{h^2}\right) \text{ and}$$

$$^*K_I = \frac{^*i'}{m.^*i} = \frac{i_1'}{m.i_1} \cdot \frac{\left(1 + \frac{K_2'}{h} + \frac{K_2'.K_3'}{h^2}\right)}{\left(1 + \frac{K_2}{h} + \frac{K_2 \,.\, K_3}{h^2}\right)} \tag{39}$$

The limit to which $^*K_I$ approximates at high h values is:

$$\frac{i_1'}{m.i_1} = K'_I \quad \text{(independent of the pH)} \tag{40}$$

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Combination of (39) and (40) now gives:

$$*K_I = K'_I \cdot \frac{(1 + \frac{K_2'}{h} + \frac{K_2' . K_3'}{h^2})}{(1 + \frac{K_2}{h} + \frac{K_2 . K_3}{h_2})} \quad (*K_I \text{ is therefore dependent on the pH}) \qquad (41)$$

If we now call $\log\ (1 + \frac{K_2'}{h} + \frac{K_2' . K_3'}{h_2}) = \varphi'$ (42)

$$\text{and } \log\ (1 + \frac{K_2}{h} + \frac{K_2 . K_3}{h_2}) = \varphi \qquad (43)$$

it follows from (41), (42) and (43) that:

$$\log *K_I = \log K'_I + \varphi' - \varphi \qquad (44)$$

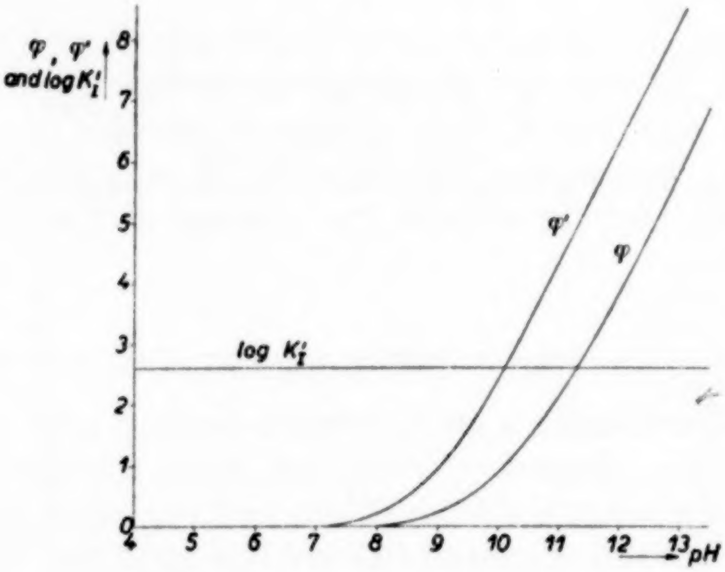

Fig. 9. φ, φ', and log K'_I as functions of the pH.

In this equation φ' and φ are "measures" of the acidity of the metal-containing and the metal-free indicator components, respectively.

According to the literature[1] the following numerical values apply for the constants used, when H_4I^- stands for the anion of murexide and M^{+2} for the calcium ion:

K_2	K_3	K_2'	K_3'	K'_I
$6.3 \cdot 10^{-10}$	$1.2 \cdot 10^{-11}$	$6.3 \cdot 10^{-9}$	$3.2 \cdot 10^{-10}$	$4 \cdot 10^2$

These data, substituted in the equations (42), (43,) and (44) furnish us with the values of φ, φ', and log $*K_I$ as functions of the pH (shown graphically in Figs. 9 and 10).

The dots are experimentally determined values for log $^*K_I$ in buffered solutions at an ion strength of 0.005 to 0.10[1]. The deviations from the theoretical values which these points exhibit are probably to be attributed to the instability of murexide in alkaline medium, particularly in the presence of calcium ions[1].

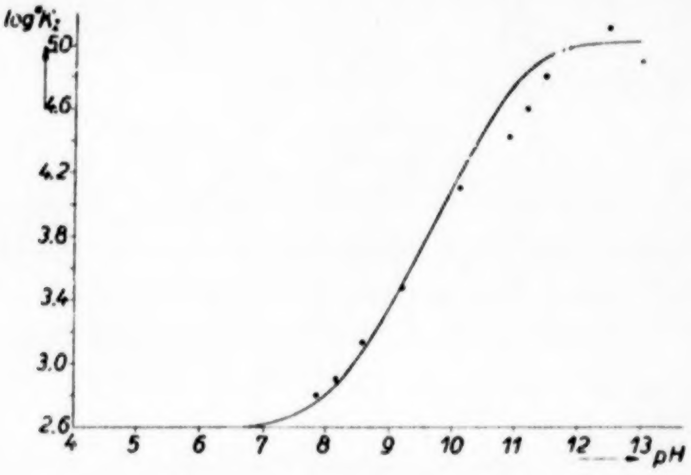

Fig. 10. The complex-forming capacity of the indicator (murexide) $^*K_I$ as a function of the pH (derived from the 3 curves of Fig. 9).

The effect of the pH on the complex-forming capacity of the titer substance $^*K_c$

When a solution containing a given complex-forming kind of ions is titrated, during this titration — dependent on the pH of the solution to be titrated — there will be formed a mixture of kinds of ions each possessing their own complex-forming capacity. Now it is of interest to know how great the "resulting complex-forming capacity" $^*K_c$ is at a given pH.

It is further assumed that per anion only one metal ion can be bound.

If we now titrate a metal ion M^{+2} with the complex-forming ion H_2Y^{-2}, the following may occur:

$$H_2Y^{-2} \rightleftharpoons H^+ + HY^{-3}$$

$$HY^{-3} \rightleftharpoons H^+ + Y^{-4}$$

$$M^{+2} + HY^{-3} \rightleftharpoons MHY^-$$

$$M^{+2} + Y^{-4} \rightleftharpoons MY^{-2}$$

Making use of the notations for $^*c$, $^*c'$, k_3, k_4, k_1', and k_2', this leads to:

$$^*c = c_3 \, . \, (1 + \frac{h}{k_4} + \frac{h^2}{k_3 \, . \, k_4}) \tag{45}$$

$$^*c' = c_3 \, . \, (k_2' + \frac{k_1'}{k_4} \, . \, h) \, . \, m \tag{46}$$

Substitution of (45) and (46) in the equation for $^*K_c$ now gives:

$$^*K_c = \frac{k_2' + \frac{k_1'}{k_4}.h}{1 + \frac{h}{k_4} + \frac{h^2}{k_3 . k_4}} \quad (^*K_c \text{ is therefore dependent on the pH}) \tag{47}$$

If we now write: $\log (k_2' + \frac{k_1'}{k_4}.h) = \Psi'$ (48)

$$\text{and } \log (1 + \frac{h}{k_4} + \frac{h^2}{k_3 . k_4}) = \Psi \tag{49}$$

then $\log {}^*K_c = \Psi' - \Psi$ (50)

If in the preceding we consider H_2Y^{-2} as the anion of complexon-III (= disodium salt of ethylenediaminetetra-acetic acid) and M^{+2} as the calcium ion, we may substitute the following numerical data[2] in (48), (49), and (50), and we can calculate the magnitudes Ψ', Ψ, and $^*K_c$ as functions of the pH (shown graphically in Figs. 11 and 12).

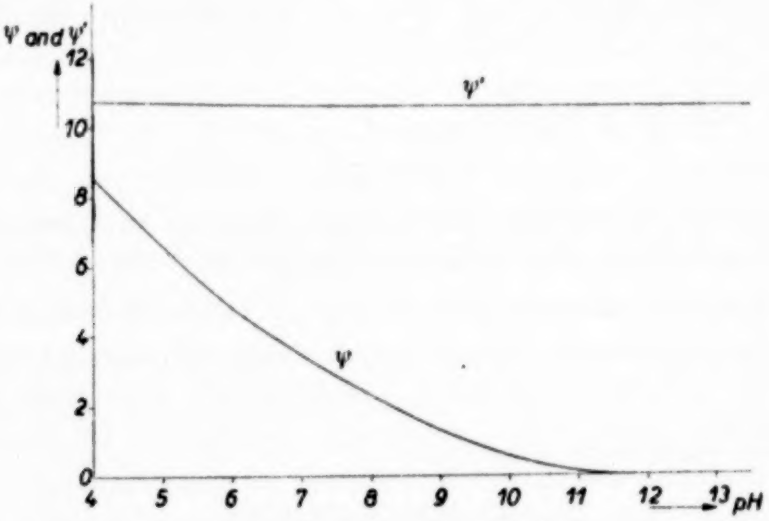

Fig. 11. ψ and ψ' as functions of the pH.

k_3	k_4	k_1'	k_2'
$6.9 \cdot 10^{-7}$	$5.5 \cdot 10^{-11}$	$3.2 \cdot 10^{3}$	$3.9 \cdot 10^{10}$

Applying these derivations to the case of Ca-murexide, the extinctions can only be calculated, if one of the following conditions is fulfilled:

1) the molar extinction coefficients of the metal-free indicator components are equal and also the molar extinction coefficients of the metal-containing

indicator components do not differ from each other in value (improbable);

2) the pH is chosen so that practical only one species of the metal-free indicator components and one of the metal-containing indicator components are present (resp. i_3 and i_3').

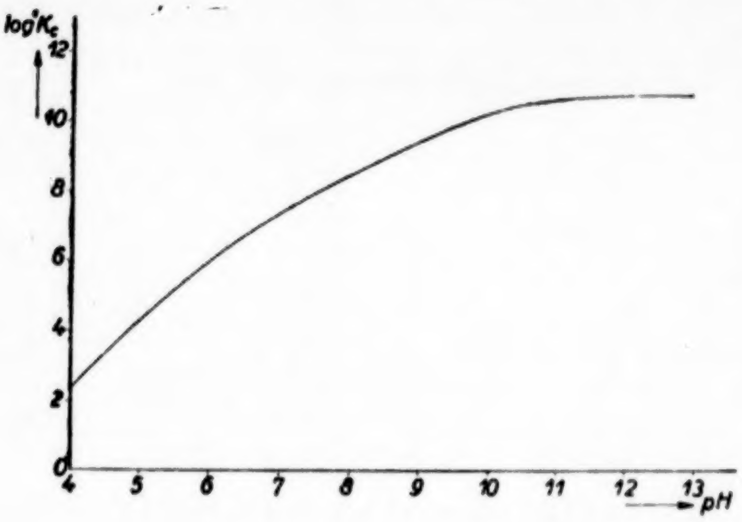

Fig. 12. The complex-forming capacity of the titer substance (complexon-III) $*K_c$ as a function of the pH.

SUMMARY

It was derived theoretically that a sharp end-point of this spectrophotometrical titration is defined, in order of importance, by:

1. $*K_c \gg *K_I$ (numerically speaking, log $\frac{*K_c}{*K_I}$ should be at least 4);
2. $*K_I$ being large (numerically *e.g.* 10^4-10^5); this is already reached by choosing a high pH;
3. i_t being low;
4. m_t being as high as possible.

RÉSUMÉ

Il a été démontré théoriquement que le point final de la titration spectrophotométrique envisagée est défini par les facteurs suivants (dans l'ordre d'importance):

1. $*K_c \gg *K_I$ (numériquement parlant log $\frac{*K_c}{*K_I}$ devrait être au moins égal à 4);
2. $*K_I$ étant grand (par exemple 10^4-10^5); ce que l'on obtient en choisissant un pH élevé;
3. i_t étant petit;
4. m_t étant aussi élevé que possible.

ZUSAMMENFASSUNG

Es wurde theoretisch abgeleitet, dass ein scharfer Endpunkt dieser spektrophotometrischen Titration in der Reihenfolge der Wichtigkeit definiert wird durch:

1. $*K_c \gg K_I$ (in Zahlen ausgedrückt soll log $\frac{*K_c}{*K_I}$ mindestens 4 sein);
2. K_I sei gross (zahlenmässig, z.B. 10^4-10^5); dies wird bereits durch die Auswahl eines hohen pH's erreicht;
3. i_t sei niedrig;
4. m_t sei so gross wie möglich.

REFERENCES

[1] G. SCHWARZENBACH AND H. GYSLING, *Helv. Chim. Acta*, 32 (1949) 1320.
[2] G. SCHWARZENBACH AND H. ACKERMANN, *Helv. Chim. Acta*, 31 (1948) 1030.

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A HIGHLY SELECTIVE PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH 8-HYDROXYQUINOLINE AND ITS APPLICATION TO THE DETERMINATION OF ALUMINIUM IN IRON AND STEEL

by

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The spectrophotometric determination of small amounts of aluminium by measuring the colour intensity of the yellow chloroform extract of aluminium hydroxyquinolate has been described by many authors.

This method was first applied by ALEXANDER[1] and then modified by MOELLER[2] and by GENTRY AND SHERRINGTON[3]. One of the most important interferences in the determination of aluminium with hydroxyquinoline is that by iron. Aluminium can be determined gravimetrically or volumetrically as aluminium quinolate in the presence of iron by using an ammoniacal solution containing tartrate and excess cyanide, ferricyanide being first reduced to non-interfering ferrocyanide. This reduction can be carried out with sulphite (LANG AND REIFER[4]), sulphide (HECZKO[5], GENTRY AND SHERRINGTON[3]), hydroxylamine (BERG[6]) or simply by boiling the alkaline solution (PIGOTT[7]). The cyanide also prevents interference by elements forming complex cyanides, as copper, nickel, cobalt, silver, cadmium and zinc. When combining this technique with the extraction procedure we found strong interference by titanium, zirconium, vanadium, manganese, lead and magnesium. For the photometric determination of aluminium in steel WIBERLEY AND BASSET[8] remove most interfering elements by electrolysis with a mercury cathode, but do not provide for the interference by vanadium and titanium. KASSNER AND OZIER[9], working in a tartrate-cyanide medium, apply a mercury cathode separation only for low contents of aluminium and tried to complex vanadium and titanium with hydrogen peroxide; in their procedure only a very limited amount of titanium (17 μg) may be present however. Neither of them mentions any interference by manganese as observed by us and also by MILLER, GEDDA AND MILISSA[10]. Recently LUKE[11] undertook a thorough investigation of the specificity of the oxine-cyanide-peroxide method and confirmed the interference by a large number of elements. We therefore came to the conclusion that no generally applicable procedure for the photometric determination of aluminium by means of hydroxyquinoline has been reported.

In the present investigation a new procedure for this determination has been developed, which allows a practically specific determination of aluminium.

DEVELOPMENT OF PROCEDURE

A search was made for a complexing agent that would make a more selective method possible. This was eventually found in ethylenediaminetetra-acetic acid (complexone, versene). Our first experiments seemed to indicate that aluminium could not be extracted from an alkaline solution (pH 8-9) containing aluminium and complexone, when shaken with a chloroform solution of hydroxyquinoline. When, however, the hydroxyquinoline was added as an alcoholic solution to the alkaline aqueous solution, it was possible to extract all the aluminium with chloroform after an hour's standing at room temperature.

Attempts to shorten this time of standing by heating the solution failed; on the contrary, if a solution containing the aluminium in the extractable form is heated by boiling and then cooled down, it again takes about one hour before the aluminium can be extracted quantitatively.

Complexone does not complex trivalent iron sufficiently to prevent the extraction of iron quinolate. It is therefore necessary to convert the iron to the ferrocyanide complex by means of cyanide and a reducing agent. As reducing agents in alkaline solution, hydroxylamine-hydrochloride, hydrazine sulphate and sodium sulphite proved to be unsuitable since any large excess of them prevented the quantitative extraction of aluminium. Hydrogen sulphide or sodium sulphide reduce very slowly and besides give rise to the precipitation of sulphides of lead, bismuth or antimony. Weak acid solutions of iron containing complexone cannot be reduced by sulphite, so that the reduction of iron has to be carried out in acid solution before the addition of complexone. Small amounts of iron ($<$ 50 mg) can be reduced by simply heating the alkaline solution, containing complexone and cyanide, to boiling; for larger amounts of iron the preliminary reduction with sulphite is necessary. Any interfering excess of sulphite is removed by boiling.

INTERFERING SUBSTANCES

In order to investigate the behaviour of foreign ions, extractions were made from solutions containing 25-100 mg of foreign ions treated according to the finally adopted procedure (solutions containing excess complexone and potassium cyanide, pH 8.5-9). Ions of the following elements were investigated:
Sb(III and V), As(III and V), Ba, Be, Bi, B (as borate), Br (as bromide), Cd, Ca, Ce(III), Cs, Cr(III), Co, Cu, F, Ga, Ge (as germanate), Au(III), I (as iodide), In, La, Pb, Li, Mg, Mn, Hg (I and II), Mo, Ni, Nb, P (as phosphate), Pt(IV), Se(IV and VI), Si, Ag, Sc, Sr, Ta, Te(IV and VI), Th, Ti, Tl, Sn(IV), W, U(VI), V(IV and V), Zn, Zr.

Amongst all these elements only Bi, Ga, In, Nb, Sb(III and V), Ta, Ti, U(VI), V(IV) and Zr are extracted as quinolates and interfere with the determination of aluminium.

Se(IV), Te(IV), Au(III) and Pt(IV) are reduced to the elemental state by the reduction with sulphite, but dissolve when complexone and cyanide are added and do not interfere.

Beryllium precipitates as the hydroxide; a small amount of beryllium is extracted in the chloroform phase as a very weakly coloured complex.

Of the common anions only fluoride in large quantities interferes.

ELIMINATION OF INTERFERENCES

As, for the determination of aluminium in steel, the most important interferences are those caused by titanium, vanadium, tantalum and niobium, interest was focussed on their elimination first. It was found that the complexes of these elements with hydrogen peroxide were not extracted by hydroxyquinoline from weak ammoniacal solution (pH 7.5-8.5). The first chloroform extract containing aluminium and these interfering elements is therefore shaken with $2N$ hydrochloric acid, causing the quinolates and the excess of hydroxyquinoline to pass into the aqueous layer. Now when an excess of hydrogen peroxide is added and the aqueous solution is made alkaline with ammonia, shaking with chloroform only extracts aluminium. It was found that in the same way aluminium could be separated from uranium.

For a generally applicable procedure the elimination of the interference by bismuth, gallium, antimony, zirconium, indium and beryllium has to be considered. The first four elements can be extracted as the cupferrates from $2N$ hydrochloric acid by chloroform. Indium can be separated from aluminium by extraction at pH 3-5 with diethyldithiocarbamate in chloroform, provided hydroxyquinoline has first been removed. Beryllium hydroxide, when in the aqueous phase, does not interfere with the extraction if a small amount of wetting agent is added. The small amount of beryllium extracted can be separated from aluminium by interposing an extraction at pH 5.

GENERAL PROCEDURE FOR THE DETERMINATION OF ALUMINIUM

Reagents

8-Hydroxyquinoline, 5% in ethanol.

Complexone III. Disodium salt of ethylenediaminetetra-acetic acid, analytical reagent.

Potassium cyanide or sodium cyanide, analytical reagent.

Ammonium bisulphite solution. Pass gaseous sulphur dioxide into $6N$ ammonia (free from aluminium) until the solution just reacts acid to litmus.

Hydrogen peroxide, 3%.

Cupferron, 6% in water, to be made fresh as needed.

Sodium acetate solution, 10%.

Sodium acetate-acetic acid-buffer pH 5. Mix 70 ml 0.2*M* sodium acetate with 30 ml 0.2 *M* acetic acid. The pH of this solution, diluted 1 : 5 with water, should be 5.0.

Sodium diethyldithiocarbamate, 2% in water, to be made fresh as needed.

Titanium solution. Dissolve potassium titanium oxalate, $K_2TiO(C_2O_4)_2.2H_2O$, analytical grade, in water, add excess sulphuric acid and heat to fuming to destroy oxalic acid. Dilute to a concentration of about 1 mg of Ti per ml and an acidity of about 2*N*.

Standard aluminium solution. Dissolve 200 mg of 99.99% aluminium metal in hydrochloric acid and dilute to 1 litre. Dilute 10 ml of this stock solution to 1 litre with 0.1*N* hydrochloric acid (1 ml = 2 μg of aluminium).

Chloroform, reagent grade. Used chloroform can be purified as follows. Shake the chloroform until colourless with concentrated sulphuric acid equal to 5 to 10% of its volume. Shake once with water and then a few times with a solution about 2*M* in both ammonia and ammonium chloride. Wash a few times with water and separate the phases as completely as possible after the last wash. Shake the chloroform with lime and leave it in contact with lime in a dark place overnight. Filter the chloroform and distil it from a waterbath, discarding the first and last fractions. Add to the receiver ethanol to make a final concentration of 1-1.5% by volume.

Apparatus

Measurements of the optical density were made with a Unicam SP500 quartz spectrophotometer.

Procedure

Take a sample containing between 2 and 100 μg of aluminium in sulphuric acid, hydrochloric acid or perchloric acid solution in a volume of about 50 ml and containing not more than 1 ml conc. nitric acid. Adjust the normality of free acid to about 1*N*, add 2 ml ammonium bisulphite* and boil the solution for 2 min. Cool and add 1 ml titanium solution if the sample contains vanadium. Add sufficient complexone (at least 1 g or about 10 times the amount of elements forming complexes with complexone), stir to dissolve and add 6*N* ammonia until just alkaline to litmus.

Add solid potassium cyanide (or the equivalent amount of sodium cyanide if large quantities of perchlorate are present) in amount equal to about 10 times the weight of all metals giving cyanide complexes, at least however 3 g, heat slowly to boiling and continue boiling for about 3 min. Cool down to room temperature, transfer the solution to a 125 ml separating funnel, add 1.0 ml* 5% alcoholic hydroxyquinoline solution while swirling and let the solution stand at room temperature for 1 hour. If a precipitate of beryllium hydroxide has formed, add a few drops of wetting agent** in order to keep the precipitate suspended in the aqueous phase.

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* If the solution contains less than 50 mg of trivalent iron, the treatment with ammonium bisulphite may be omitted, as small amounts of iron are reduced by boiling the alkaline solution containing complexone and cyanide.

After that time add 10 ml chloroform and shake 1 min. Draw off the chloroform layer into a second separating funnel and continue extracting with 5 ml portions of chloroform until any quinolate precipitate has gone into solution and the last but one extract is absolutely colourless. In most cases 3-4 extractions will be sufficient.

Wash the combined chloroform extracts by shaking with 25 ml of water and run off the chloroform solution into a clean separating funnel; wash the aqueous layer with 5 ml of chloroform which are added to the main chloroform extract and discard the aqueous layer. Add 25 ml 2*N* hydrochloric acid to the chloroform solution and shake vigorously for 1 min. Draw off the chloroform and discard it***.

The hydrochloric acid solution thus obtained is treated according to A or to B, depending on whether beryllium is present or absent.

A. *Beryllium present*

Add to the hydrochloric acid solution a few drops of methyl orange and conc. ammonia until the colour of the indicator just turns yellow, add 5 ml acetate buffer pH 5, 10 ml of chloroform and shake 1 min. Draw off the chloroform extract in a clean separating funnel and extract the aqueous solution again twice with 5 ml of chloroform. The aqueous solution is discarded. Shake the combined chloroform solutions with 25 ml 2*N* hydrochloric acid for 1 min. Draw off the chloroform and discard it. Continue according to B.

B. *Beryllium absent*

Add to the hydrochloric acid extract 20 ml 3% hydrogen peroxide and a few drops of phenol red and after 1 min. add 6*N* ammonia until the colour of the indicator has just completely changed from yellow to red. Add 10 ml of chloroform and shake 1 min. Proceed according to C, D, E or F depending on the presence or absence of bismuth, antimony, zirconium, gallium or indium.

C. *Bi* $<$ 0.5 *mg, Sb* $<$ 0.1 *mg; Zr, Ga, In absent*

Draw off the chloroform layer into a 25 ml volumetric flask. Repeat the extraction with two 3-5 ml portions of chloroform which are collected in the volumetric flask and finally dilute to volume with chloroform. Filter the chloroform solution through a small dry filter (*e.g.* Whatman No. 40) into the appropriate absorption cell, discarding the first 5 ml. Measure the optical density at 390 mμ on a spectrophotometer against pure chloroform. Subtract the optical density of a blank carried out with all reagents and determine the amount of aluminium from a previously prepared calibration curve.

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* If necessary add more hydroxyquinoline solution if large amounts of elements precipitating in complexone-cyanide solution are present. Excess reagent can be judged after some practice by the orange colour of the solution.

** We used Tergitol (Carbide and Carbon Chemicals).

*** If large amounts of quinolates were extracted it is advisable to draw off the chloroform in a separating funnel and to shake again with 10 ml 2*N* hydrochloric acid before discarding it. This second acid wash is combined with the first one.

Determine 10-100 μg of aluminium in a 1-cm cell
,, 5-50 μg ,, ,, ,, ,, 2-cm ,,
,, 2-25 μg ,, ,, ,, ,, 4-cm ,,

D. *Zr, Ga present; Bi* $>$ 0.5 *mg; Sb* $>$ 0.1 *mg; In absent*

Draw off the chloroform layer into a separating funnel and repeat the extraction with two 3-5 ml portions of chloroform. To the combined chloroform extracts add 25 ml $2N$ HCl and shake 1 min. Draw off the chloroform layer and discard it. Add to the hydrochloric acid solution 5 ml 6% cupferron solution, mix and add 10 ml chloroform. Shake 1 min, draw off and discard the chloroform after separating the layers. Repeat this extraction with 5 ml portions of chloroform until any insoluble cupferrate has dissolved. If necessary add more cupferron. Run off the hydrochloric acid solution into a 100 ml beaker, add 1 ml concentrated sulphuric acid and 1 ml nitric acid and evaporate to fumes of sulphuric acid, adding a few drops of nitric acid if the sulphuric acid darkens on fuming. Cool, dilute with 20 ml of water and transfer the solution to a separating funnel, washing the beaker with a small quantity of water. Add to the sulphuric acid solution 1.0 ml 5% hydroxyquinoline and a few drops of phenol red. Add $6N$ ammonia until the colour of the indicator has just changed completely from yellow to red. Cool if necessary and extract, first with 10 ml of chloroform, then with two 3-5 ml portions of chloroform and catch the extracts in a 25 ml volumetric flask. Dilute to volume with chloroform. Filter the solution through a small dry filter into the appropriate absorption cell, discarding the first 5 ml. Measure at 390 mμ as described under C. Carry a blank through the whole procedure.

E. *In present; Zr, Ga absent; Bi* $<$ 0.5 *mg; Sb* $<$ 0.1 *mg*

Draw off the chloroform layer into a separating funnel and repeat the extraction with two 3-5 ml portions of chloroform. To the combined extracts add 25 ml $2N$ HCl and shake for 1 min. Draw off the chloroform layer and discard it. Add to the hydrochloric acid solution excess saturated bromine water (ca 8 ml) and extract dibromohydroquinoline and excess bromine with chloroform until the last chloroform extract is absolutely colourless. Add 1 to 2 drops of methyl orange, 3 ml 10% sodium acetate and adjust the pH to about 4 with ammonia. Add 10 ml 2% sodium diethyldithiocarbamate, mix and extract twice with 10 ml chloroform. If a precipitate forms on adding the carbamate, first extract with chloroform until it has completely disappeared. Discard the chloroform extracts, run the aqueous layer into a 100 ml beaker, add 10 ml 6*N* HCl and boil a few minutes to destroy the carbamate. Cool, transfer to a separating funnel, add 1 ml 5% hydroxyquinoline and 5 drops of phenol red and add 6*N* ammonia until the colour of the solution has completely turned red. Finish the determination by extraction with chloroform as described under D.

F. *In present: Zr, Ga present; Bi > 0.5 mg; Sb > 0.1 mg*

Proceed according to D, up to the point where the aqueous solution containing cupferron has been fumed with sulphuric acid. Dilute the sulphuric acid residue with 25 ml of water, add 1-2 drops of methyl orange, 3 ml 10% sodium acetate and adjust the pH to about 4 with ammonia. Perform an extraction with diethyldithiocarbamate and finish the determination as under E.

DISCUSSION

pH. In accordance with previous authors we found extraction to be quantitative in the pH range 7-9.5. In the first extraction a pH of 8.5-9.5 is obtained; the pH automatically adjusts itself in this range because of the strong buffering action of complexone. In the second extraction the pH is adjusted by means of phenol red to 7.5-8.

Wavelength. Different values for the wavelength of maximum absorption have been reported in the literature: 385 mμ (MARGERUM, SPRAIN AND BANKS)[12]; 389 mμ (KASSNER AND OZIER)[9]; 390 mμ (WIBERLEY AND BASSETT)[8]; 395 mμ (ALEXANDER,[1] MOELLER[2], GENTRY AND SHERRINGTON[3]). We found maximum absorption at 388 mμ. A wavelength of 390 mμ was chosen for our measurements, as below 390 mμ the absorption of hydroxyquinoline in chloroform quickly increases. An aluminium-free solution shows an optical density of about 0.015 in a 2-cm cell at 390 mμ when measured against pure chloroform.

Amount of reagent. The amount of reagent given in the procedure (1 ml 5% quinoline) is adequate for the precipitation of about 5 mg Ti, Zr, V, etc. If larger amounts of precipitable elements are present the amount of reagent should be increased accordingly. If section C is followed, a blank should be carried out using the same amount of reagent.

Standing time. Solutions containing 20-50 μg of aluminium, 1 g of complexone, 3 g of potassium cyanide and 1 ml of 5% hydroxyquinoline were extracted with chloroform. Measurements of the amount of aluminium extracted after standing times at room temperature of 15, 30, 45, 60 and 90 min, respectively, gave 50%, 60-70%, 85-90%, 100%, 100% of aluminium recovered. It was concluded that a standing time of one hour is sufficient.

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Volume of solution to be extracted. Experiments indicated that the volume of the complexone-cyanide solution could vary between 50 and 200 ml, without preventing quantitative extraction of aluminium.

Effect of vanadium. If vanadium is present in the sample this is extracted very slowly previous to aluminium, making a large number of extractions necessary in order to extract all aluminium. It was found, however, that, in the presence of 0.5-1 mg of titanium, vanadium and aluminium are extracted very quickly. Thus in the presence of vanadium addition of titanium is indicated, unless already present in the sample. Vanadium in the pentavalent condition is not extracted; the preliminary reduction with sulphite or the boiling of the alkaline solution, however, reduces vanadium to the tetravalent state.

Reduction of iron. For the reduction of iron in acid solution we found ammonium bisulphite to be the best reagent. By heating the solution to boiling the greater part of the excess sulphite is volatilized. As mentioned before, small amounts of iron ($<$ 50 mg) are reduced by boiling the alkaline complexone-cyanide solution. Large amounts of phosphoric acid ($>$ 200 mg) prevent the reduction of iron by ammonium bisulphite in acid solution and also prevent reduction in alkaline solution.

Amount of complexone and cyanide. The amounts of these reagents as given in the procedure have proved to be adequate.

For 0.1 g of iron or steel use 1 g complexone and 3 g KCN.
For 0.5 g of iron or steel use 3 g complexone and 5 g KCN.
For 1.0 g of iron or steel use 8 g complexone and 8 g KCN.
To complex manganese at least 20 times the amount of complexone is necessary.

Effect of interfering elements. Known quantities of aluminium were extracted from complexone-cyanide solution containing diverse amounts of the interfering elements and the error determined in terms of micrograms of aluminium, when measured at 390 mμ. The results are given in Table I.

TABLE I

ELEMENTS EXTRACTED AS QUINOLATE FROM ALKALINE COMPLEXONE-CYANIDE SOLUTION

Vanadium	100 μg V(IV)	∿	7 μg Al
Titanium	10 μg Ti	∿	4 μg Al
Zirconium	10 μg Zr	∿	10 μg Al
Uranium	200 μg U	∿	5 μg Al
Gallium	10 μg Ga	∿	10 μg Al
Indium	10 μg In	∿	3 μg Al
Bismuth	1 mg Bi	∿	1.6 μg Al
Antimony	1 mg Sb	∿	11 μg Al

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It is seen that only bismuth and antimony do not interfere in microgram quantities. Beryllium is only extracted to a very small amount. Up to 15 μg of beryllium do not interfere seriously. For larger amounts of beryllium up to 5 mg the aluminium errors increase slowly from 5 to 25 μg.

Effect of thorium. Thorium in amount up to 25 mg has no effect on the determination of aluminium. Larger quantities of thorium, however, prevent the quantitative extraction of aluminium; with 100 mg of Th present *e.g.*, no aluminium is extracted at all. In these solutions a large amount of hydroxyquinoline gives a precipitate of thorium quinolate.

Effect of scandium. In the presence of scandium, sufficient hydroxyquinoline has to be added to combine with all the scandium as otherwise no aluminium is extracted. Using 1 ml of 5% hydroxyquinoline the maximum amount of scandium is 1 mg.

Effect of anions. The common anions, as chloride, sulphate, perchlorate, acetate, bromide, iodide, do not interfere, as is already known from previous work (GENTRY AND SHERRINGTON, WIBERLEY AND BASSET). Nitric acid interferes when exceeding 1 ml of conc. acid, by preventing total reduction of iron. Fluoride interferes in amounts greater than 10 mg by preventing the extraction of aluminium. Addition of boric acid does not decrease this interference. Phosphoric acid in quantities greater than about 200 mg interferes by preventing the reduction of iron.

Reagent blank. The reagent blank is normally of the order of 1-2 μg of aluminium. High blanks can be caused by a high aluminium content of potassium or sodium cyanide and cupferron. Some cupferron samples contained large amounts of aluminium, presumably because of the use of aluminium for the reduction phase in its preparation. A sample from Merck contained only 2 p.p.m. of aluminium. Potassium or sodium cyanide, if containing aluminium, can be purified as follows: dissolve 10 g of KCN or NaCN in 100 ml of water, add 5 g sodium bisulphate in order to decrease the pH, add 1 ml 5% hydroxyquinoline and extract with chloroform until free from aluminium. In place of solid cyanide an equivalent aliquot of these solutions is used.

When determining very small amounts of aluminium it is advisible to perform all boiling and fuming operations in quartz or Vycor vessels.

Calibration curves. Prepare a series of solutions containing 0, 5, 10, 20, 40, 60, 80 and 100 micrograms of aluminium in a volume of about 50 ml, containing 25 ml $2N$ hydrochloric acid, add a few drops of phenol red and 1.0 ml 5% hydroxyquinoline. Add $6N$ ammonia until the indicator turns red and extract first with 10 ml of chloroform and then with two 5 ml portions of chloroform. Catch the chloroform extracts in a 25 ml measuring flask and dilute to volume with chloroform. Filter the solutions through a dry filter in the appropriate absorption cells. Measure the solutions containing aluminium against the solution without aluminium at 390 mμ and plot optical density against amount of aluminium.

The plots for 1-, 2- and 4-cm cells were straight lines up to an optical density of about 1.0.

RESULTS

This procedure has been applied succesfully to synthetic solutions (Table II) and to a number of standard samples (Table III).

TABLE II

SYNTHETIC ALUMINIUM SOLUTIONS

Elements added	Aluminium present μg	Aluminium found μg
100 mg Fe, 20 mg Co, 20 mg Cu, 5 mg Ti	20	19.5
100 mg Fe, 20 mg As(V), 5 mg each Mn, Mg, Ti	20	21
100 mg Fe, 20 mg Cr, 10 mg Ni, 5 mg Mn, 5 mg Ti	20	20
100 mg Fe, 100 mg Zn, 20 mg each Pb, Cd, Mo, Ni, Cr 10 mg each Ag, Mn, 5 mg each Ba, Mg, Ti, 1 mg V	20	20.5; 19.5
100 mg Fe, 100 mg La, 100 mg Sr, 25 mg each Ce, Pt, Cs	20	19
100 mg Fe, 5 mg each U, Mn, 1 mg each Ti, V	20	21
100 mg Fe, 5 mg Ga	25	24
100 mg Fe, 5 mg In	25	24.5
100 mg Fe, 20 mg Zr	15	15
100 mg Fe, 3 mg each Bi Sb	25	25
200 mg Fe, 20 mg Mn 2 mg each U, Zr, V, Ga, In, Bi, Sb, Ti	20 25	17, 18, 22, 23 23
100 mg Fe, 20 mg Cr, 10 mg Ni, 1 mg each Ti, Ta, Nb, V	16	16; 17
200 mg Fe, 20 mg Mn, 25 mg Th	10	10.5; 10
	100	100
100 mg Fe, 25 mg Ce, 10 mg each Th, Hg(II), Te, Tl, Ge	20	21
500 mg Cu, 5 mg each Fe, Mn, Ni, Co	20	19.5
500 mg Mo (as molybdate), 5 mg each Fe, Mn, Ni, Co	10	10
1000 mg W (as tungstate), 5 mg each Fe, Mn, Ni, Co	20	20
300 mg $Ca_3(PO_4)_2$, 10 mg each Fe, Mn, Mg	20	20.5
2 g Se (as selenate), 20 mg Fe, 10 mg Mn	10	9
25 mg Fe, 50 mg Sn, 25 mg Mn	10	9.5; 11
10 mg Fe, 100 mg Au, 10 mg Mn	10	10; 10
100 mg Fe, 20 mg Be, 10 mg Mn, 1 mg Ti, 1 mg V	20	19
100 mg Fe, 1 mg Sc	20	19.5

TABLE III

ANALYSIS OF BUREAU OF STANDARDS SAMPLES

Sample No.		sample weight or aliquot	certified value and range %		exptl. value %
93	Borosilicate glass	4 mg	1.94	(1.91-1.94)	1.9^6; 2.0^0 Al_2O_3
89	Lead-barium glass	50 mg	0.18	(0.12-0.18)	0.16^5; 0.17^0 Al_2O_3
80	Soda-lime glass	25 mg	0.33	(0.24-0.44)	0.30; 0.29; Al_2O_3
63	Phosphor bronze bearing metal.	50 mg	0.05	(0.04-0.07)	0.040; 0.041; 0.041; 0.042 Al
94a	Zn-base die casting alloy	1 mg	3.90	(3.88-3.95)	3.9^0; 4.0^0 Al
88	Dolomite	100 mg	0.067	(0.064-0.069)	0.067; 0.067 Al_2O_3

Treatment of glass samples: silica eliminated by means of hydrofluoric and sulphuric acids, residue fused with bisulphate and extracted with acid.

Application to iron and steel

Solution of samples. For the determination of acid-soluble aluminium the sample is dissolved in sulphuric acid (1 : 9) or hydrochloric acid (1 : 1) and oxidized by a slight excess of nitric acid. After filtering the solution procedures B and C are applied, which provide for the presence of vanadium and titanium. For zirconium-containing steels procedure D should be followed. If the determination of total aluminium is called for, the residue obtained on filtering the steel solution is ashed, fumed with hydrofluoric and sulphuric acids and fused with bisulphate. The melt is dissolved in dilute sulphuric acid and combined with the main filtrate.

Tungsten-containing steels are treated with hydrochloric or sulphuric acids and nitric acid until the separated tungsten oxide is bright yellow; this can either be filtered off or left in the solution as it dissolves completely on adding complexone and cyanide.

Size of sample. For aluminium in excess of 0.01% use a 0.1 g sample, and if necessary, an aliquot of the suitably diluted solution; use 1 g of complexone and 3 g of potassium cyanide. For aluminium below 0.01% use a 0.5 to 1 g sample with the amounts of complexone and cyanide given above: reduce with 10 ml of ammonium bisulphite.

Results. The results obtained with a number of steel standard samples are given in Table IV.

SUMMARY

Aluminium hydroxyquinolate can be quantitatively extracted by chloroform from an ammoniacal solution containing hydroxyquinoline, complexone and cyanide. Likewise extracted are titanium, vanadium, tantalum, niobium, uranium, zirconium,

TABLE IV

ANALYSIS OF STEEL

Sample No. NBS = National Bureau of Standards BCS = British Chemical Standards			Sample weight or aliquot	certified value and range % Al t = total a.i. = acid insoluble a.s. = acid soluble		Al found %
NBS	55c	Ingot iron	1 g	0.003	t	0.003; 0.003
NBS	22c	Bessemer steel	100 mg	0.116 (0.106-0.126)	t	0.11; 0.11
NBS	100a	Manganese steel	100 mg	0.040 (0.039-0.042)	t	0.036; 0.040; 0.040; 0.038
NBS	125	High silicon steel	10 mg	0.261 (0.251-0.270)	t	0.25; 0.25; 0.26; 0.26
NBS	106a	Cr-Mo-Al steel	4 mg	1.08 (1.07-1.12)	t	1.09; 1.11; 1.12; 1.14
NBS	106a	Cr-Mo-Al steel	100 mg	0.011 (0.010-0.012)	a.i.	0.014; 0.014; 0.014; 0.014
NBS	6e	Cast iron (0.024% V; 0.025% Ti)	100 mg	—	a.s.	0.0052; 0.0057
NBS	6e	Cast iron added 0.010%	100 mg	—	a.s.	0.015; 0.016
NBS	132	Mo-W-Cr-V steel (6.3% W, 7.07% Mo, 4.1% Cr, 1.64% V)	100 mg	—	a.s.	0.012
NBS	132	id. added 0.010%	100 mg	—	a.s.	0.021
NBS	61	Ferrovanadium (31.1% V)	20 mg	0.02 (0.01-0.03)	t	0.027; 0.028; 0.032; 0.034
NBS	116	Ferrotitanium (25.5% Ti)	0.75 mg	5.51 (5.46-5.58)	t	5.5; 5.6
BCS	233	Permanent Magnet steel (24% Co; 11% Ni; 5% Cu; 0.8% Ti)	1 mg	6.98 (6.89-7.08)	a.s.	7.1; 7.0

gallium, antimony, bismuth, indium and traces of beryllium. Aluminium can be separated from the first five elements by an extraction in ammoniacal solution containing hydrogen peroxide.

Zirconium, gallium, bismuth and antimony can be eliminated by a cupferron extraction and indium by extraction with diethyldithiocarbamate. Beryllium is eliminated by performing an extraction with hydroxyquinoline at pH 5. The proposed method enables a practically specific photometrical determination of aluminium. Applications are given of the determination of trace and higher amounts of aluminium in steels, non-ferrous alloys and in glass.

RÉSUMÉ

L'hydroxyquinoléate d'aluminium peut être extrait quantitativement par le chloroforme, en solution ammoniacale renfermant de l'hydroxyquinoléine, du complexon et du cyanure. Sont également extraits: titane, vanadium, tantale, niobium, uranium, zirconium, gallium, antimoine, bismuth, indium et traces de béryllium. L'aluminium peut être séparé des 5 premiers éléments par extraction en solution ammoniacale, en présence de peroxyde d'hydrogène. Zirconium, gallium, antimoine et bismuth peuvent être éliminés par extraction au moyen de cupferron et l'indium par extraction au diéthyldithiocarbamate. Le béryllium est éliminé par extraction avec l'hydroxyquinoléine au pH 5. Ce procédé permet un dosage photométrique pratique et spécifique de l'aluminium. Des applications sont proposées pour le dosage de traces et de plus fortes teneurs en aluminium, dans les aciers, les alliages non ferreux et le verre.

ZUSAMMENFASSUNG

Aluminiumhydroxychinolat kann quantitativ mit Chloroform extrahiert werden aus einer Lösung, die Hydroxychinolin, Komplexon und Cyanid enthält.

Ebenfalls extrahiert werden: Titan, Vanadin, Tantal, Niob, Uran, Zirkon, Gallium, Antimon, Wismut, Indium und Spuren von Beryllium. Aluminium kann von den ersten fünf Elementen getrennt werden durch eine Extraktion in ammoniakaler, peroxydhaltiger Lösung.

Zirkon, Gallium, Antimon und Wismut können durch eine Extraktion mit Kupferron entfernt werden und Indium durch Extraktion mit Diäthyldithiocarbamat. Beryllium wird durch Extraktion mit Hydroxychinolin bei pH 5 entfernt. Das vorgeschlagene Verfahren ermöglicht eine praktisch spezifische photometrische Bestimmung von Aluminium.

Es werden Anwendungen gegeben für die Bestimmung von Spuren und höheren Gehalten an Aluminium in Stahl, Nichteisenlegierungen und Glas.

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THE DETERMINATION OF THE NUMBER OF ELECTRONS INVOLVED IN IRREVERSIBLE REDUCTIONS BY MICROCOULOMETRY

by

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INTRODUCTION

A number of methods are available for the determination of "n", the number of electrons involved in a unit of reaction at the dropping mercury electrode. If the reduction is reversible, measurement of the slope of a graph obtained by plotting log i/i_d-i against E (where E is the applied potential and i and i_d are the diffusion current flowing at voltage E and the maximum diffusion current respectively) may be employed[1]. This gives satisfactory results unless the number of electrons is large, when slight errors lead to large variations in the value for n. If the diffusion coefficient of the reacting species is known confirmation of n can be obtained from the Ilkovic equation and this latter method may also be applied, in many cases, to irreversible reactions. If the diffusion coefficient is not known and the reaction is irreversible, several n values may be assumed and the diffusion coefficient corresponding to each calculated. Examination of the values obtained will often lead to the elimination of incorrect n values because of the absurdity of the calculated diffusion coefficient.

Only the first of the methods outlined above gives satisfactory results and the third is always open to suspincion. Coulometric methods, especially those carried out under actual polarographic conditions, are to be preferred in the case of irreversible reactions. The latter technique, termed microcoulometry, is discussed in detail in this paper.

The use of coulometry on a macro scale is now a well-established practice. As developed by LINGANE and others[2] it consists of electrolysing a solution at a stirred mercury pool cathode and employing a coulometer such as the hydrogen, silver or iodine coulometer to integrate the current passed. The constant potential difference between the cathode and standard electrode is maintained throughout the electrolysis either by constant manual adjustment or by means of an automatic device, such as a potentiostat[3]. The initial and final concentrations of reacting ion species are usually determined polarographically and the number of electrons involved in the reduction is calculated by means of Faraday's laws.

The mechanisms of a number of reactions have been elucidated by this technique[4,5], but there is the danger that the reaction occurring at the large stirred, mercury surface may not be identical with that which occurs at the dropping mercury electrode. To avoid this difficulty the present work was carried out with the object of developing a satisfactory microcoulometric technique, in which the electrolysis was carried out at the dropping mercury electrode itself.

A number of previous attempts to use microcoulometric techniques of this type have met with little success, mainly due to the erratic changes in the current flowing during the electrolysis, caused, almost certainly, by fluctuation of the concentration of reducible ion around the dropping electrode. Two papers, however, which came to hand during our investigations describe the successful use of coulometry at the dropping mercury electrode. GILBERT AND RIDEAL[6] describe a technique which is substantially the same as that developed by us, but no critical examination of the conditions governing successful operation of the method is reported. Results for cadmium and an azo dye are given. BOGAN, MEITES, PETERS AND STURTEVANT[7] describe an electronic apparatus for the integration of the current passing during the electrolysis of a small volume of solution. Results for the reduction of thallium, lead and cadmium are reported and the average accuracy and precision obtained appears to be about 3 per cent. An attempt by LINGANE AND LOVERIDGE to integrate the current-time curve was also mentioned in this paper and it was indicated that little success was obtained; they attributed this to the depletion of the reducible ion around the capillary tip as the electrolysis proceeded.

We considered that the construction of a complicated electronic apparatus was undesirable if the work was to be generally applicable and we therefore decided to employ a polarograph to apply the potential difference across the electrodes and also to act as a coulometer.

BASIC PRINCIPLES

Before describing the apparatus employed and discussing the results obtained it is desirable to give the basic equations applicable to coulometry and an outline of the different methods of obtaining and calculating results.

From Faraday's laws the following equation is obtained:

$$n = \frac{M}{F} \times \frac{X}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1.$$

Where: — M = The molecular weight of the reacting substance
F = The Faraday (96,500 coulombs)
X = The number of coulombs passed during the electrolysis
W = The weight (in grams) of the substance that has reacted

Also, from Faraday's laws and the Ilkovic equation it may be shown that: —

$$i_t = i_0 \times e^{-Kt/n} \quad \ldots \ldots \quad 2$$

Where: — i_0 = The limiting diffusion current at the start of the electrolysis
i_t = The limiting diffusion current after electrolysis for a time t
and K = a constant.

To obtain a value for n from equation 1 it is necessary to determine W and X. This may be done in a number of ways.

1. As already stated W is usually evaluated by measuring the initial and final concentrations polarographically. Thus, if i_0 and i_t are the initial and final diffusion currents measured:

$$W = \frac{i_0 - i_t}{i_0} \times V \times C \quad \ldots \ldots \quad 3$$

Where: V = The volume of the solution electrolysed
C = The initial concentration of the reacting substance

Since:

$$X = i_{av} \times t \quad \ldots \ldots \quad 4$$

Where: i_{av} = the average current flowing during the electrolysis and it can be shown that: —

$$i_{av} = \frac{i_0 - i_t}{2.3 \log i_0/i_t} \quad \ldots \ldots \quad 5$$

It is therefore only necessary to measure the initial and final diffusion currents in order to calculate n.

The arithmetic mean of the initial and final diffusion currents $\frac{i_0 + i_t}{2}$ is a very close approximation for the true average current, i_{av}, and this expression may therefore be substituted without serious loss of accuracy. In fact, if i_t has fallen to 75 per cent. of i_0 the error involved is less than 1 per cent. and even with a 50 per cent. reduction it remains less than 5 per cent. The equation for calculating n may therefore be reduced to:

$$n = \frac{M}{F} \times t \times \frac{i_0 + i_t}{i_0 - i_t} \times \frac{i_0}{2 \times V \times C} \quad \ldots \ldots \quad 6$$

In this expression:

i_0 and i_t are in microamps
V is in ml
C is in microgram per ml
t is in seconds.

If, instead of taking only an initial and final polarogram, a number of polarograms are recorded at intervals in the electrolysis then any two values of the diffusion current obtained, together with the corresponding time interval, may be substituted in equation 6. In this way a number of values for n may be obtained for a single electrolysis (*e.g*, five polarograms yield ten results) and the average taken. We have called this method the Arithmetic Average Method.

2. It is possible, with the majority of recording polarographs, to arrange that the recording drum rotates while the potential difference applied to the cell electrodes remains constant. Such a polarograph may therefore be used to obtain a continuous record of the current flowing throughout the electrolysis. The value of X may thus be obtained directly from the area under the current-time curve obtained and substituted in equation 1. W must still be evaluated by recording polarograms before and after electrolysis and these may also be used to provide a second result by the method already described (equation 6). This method has been termed the Integration Method.

3. A further method, called the Graphical Method, is based on the following: Consider equation 2. Taking logarithms:

$$\log i_t = \log i_0 - \frac{K.t}{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 7$$

The slope of a graph of log i against t is therefore proportional to n and if i is measured in arbitrary scale divisions and $\log_{10} i$ plotted against t in seconds:

$$\text{Slope} \times n = \frac{K_2}{K_1} \times \frac{0.4343}{F \times V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 8$$

Where: K_1 = Concentration in moles/litre which gives a step height of one division
K_2 = Current in amps equivalent to one division
F = The Faraday
V = Volume in litres of the solution electrolysed

The values of current at each time interval may either be obtained by recording polarograms at intervals during the electrolysis, as in the Arithmetic Average Method, or they may be read off a current-time curve recorded as outlined in the integration method above.

Sources of error

There are a number of possible sources of error inherent in the above methods of obtaining and calculating results. The errors in the measurement of current, time and volume of solution should be very small (less than 3 per cent.) but those due to the conditions under which the measurements are made may be large. The most serious errors arise as a consequence of depletion of the reacting species around the mercury drop. At the commencement of the electrolysis removal of ion at the drop surface is replaced by the normal processes of diffusion from the main bulk of the solution and the diffusion gradient is of normal size[8]. However, as the electrolysis proceeds the main bulk of the solution itself becomes increasingly depleted in the region of the dropping electrode so that the depleted layer becomes very wide. In the absence of stirring the concentration of reducible ion in the main bulk of the solution is therefore no longer uniform and a continuous record of the current flowing, while remaining a true measure of the coulombs passed, will not be proportional to concentration. Similarly, if a series of polarograms are taken at intervals after stirring the solution, a true record of the concentration of the reacting ion at given times will be obtained, but the current will not necessarily fall exponentially between successive determinations.

It is obvious from these considerations that only the integration method provides a simultaneous, continuous record of the current actually flowing, together with the weight of the substance electrolysed by it. It is therefore to be expected that it will be the most accurate method. Moreover, the other methods rely upon the assumption that the current falls exponentially during the electrolysis and are therefore liable to error.

APPARATUS

A special research, photographically-recording polarograph, constructed in these laboratories[9] was used for this work. This instrument has two speeds of rotation of the potentiometer and camera drum, the slower being 45 minutes for complete rotation. The auxiliary potentiometer control incorporated in this instrument may be set so that the same potential is applied to both ends of the main potentiometer. A steady potential difference is therefore applied to the cell electrodes and this is not altered by rotation of the main potentiometer and camera drum. The slow-speed was used for electrolyses throughout this work and a suitable steady potential was selected when determinations were being made by the integration method. For this method the function of the polarograph is merely to provide a continuous record of current passing in a given time at a steady potential difference. It should be emphasised, however, that any polarograph which is capable of applying a steady potential while the recording apparatus is functioning at a slow speed may be used for this type of determination. The Cambridge photographic and pen-writing polarographs are suitable.

The special conditions obtaining in this type of determination necessitated the design of a cell in which small volumes of solutions could be polarographed. The cell employed is shown in Fig. 1. The inner tube, A, has an internal diameter of 6 mm which is small enough to allow electrolysis and polarography to be carried out on volumes of solutions as small as 0.2 ml, while just permitting easy access to the dropping mercury electrode, D, and the silver anode, E. The small holes, C, in the lower end of this tube give access to the outer jacket, B, so that mercury may fall into the pool for a considerable period without causing an undue rise in level. The outer jacket, B, is flanged and is of such diameter that it just fits into one of the holes in the turntable of a Cambridge polarographic thermostat bath. The water-sealed sleeve, G, prevents the entry of atmospheric oxygen and the tube, F, allows hydrogen to be passed in during the electrolysis. In practice the passage of hydrogen during electrolysis was not found to be necessary due, presumably, to the very small surface area of the solution and the comparatively high concentration of reducible ion that was ultimately used.

The silver anode, E, is a piece of wire beaten flat and shaped to a vertical cylinder of such diameter that it just fits round the end of the dropping mercury electrode. When it was desired to use the mercury pool as an anode, connection was made by dipping a platinum wire into the mercury in the outer tube.

It was found that smoother current-time curves were obtained with a capillary of much thinner wall than is normally used. This type of capillary (Fig. 1) was prepared by drawing out a polarographic capillary of normal wall thickness, but having a drop-time of about one second. The external diameter was reduced from about 5 mm to 1-2 mm, when the drop time in N potassium chloride was 3-4 seconds.

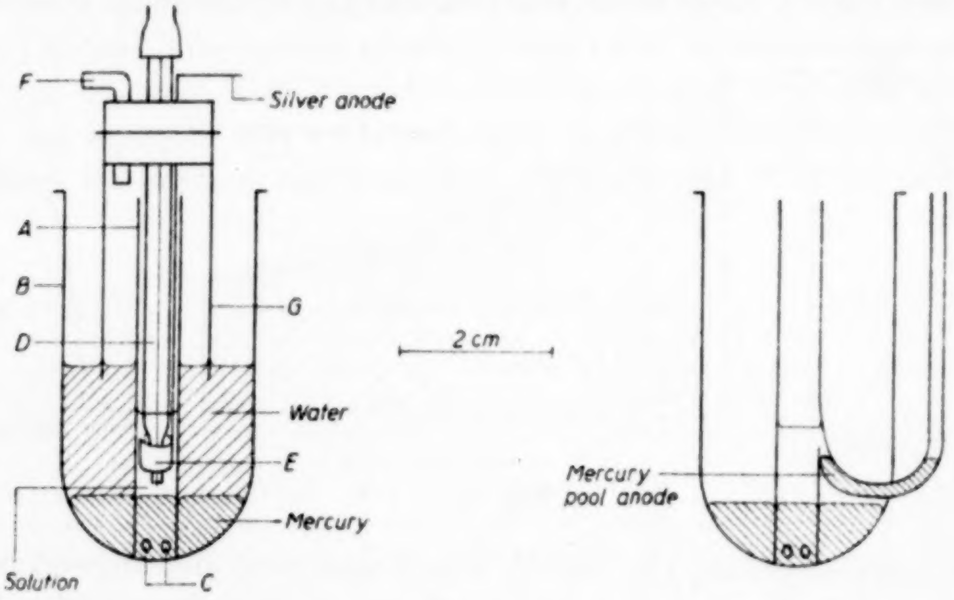


Fig. 1.

EXPERIMENTAL

All determinations were carried out at 25° C and the microcell was usually placed in the thermostat bath about an hour before the commencement of the electrolysis. This allowed the cell and mercury to attain the bath temperature. Meanwhile an aliquot of the solution to be examined was placed in an ordinary polarographic cell, deoxygenated and polarographed. From this polarogram a suitable potential for the electrolysis was selected, usually about 0.2 volts more negative than the half-wave potential of the step recorded and the voltage across the cell electrodes was adjusted to this value. If necessary the galvanometer zero was adjusted so that the spot was on a suitable part of the screen and the polarograph battery was then switched off.

After a final deoxygenation a small portion of the solution in the polarographic cell was transferred to the microcell by means of a graduated 1 ml pipette. The size of aliquot necessary to give a reasonable decrease in concentration in the period of electrolysis was determined by a trial experiment.

The washed and dried dropping electrode and the silver anode (when used) were lowered into the microcell and the battery and a stopwatch were switched on simultaneously. The progress of the electrolysis was observed by watching the polarograph scale.

When the integration method was being employed a record of the current-time curve was made on the polarograph camera with the polarograph set to run at 'slow speed' (see Fig. 2). No external damping of the galvanometer and no counter current were applied during the record, which was generally allowed to proceed for 45 minutes. A further polarogram was then recorded after stirring by means of bubbling hydrogen through the solution. The hydrogen was passed in through a fine, thin-walled capillary dipped into the solution. To calculate the result obtained the area under the curve was first evaluated as follows. The zero-current line of this curve on the photographic record was found by marking a point vertically below the beginning of the curve and at a distance equal to the step-height

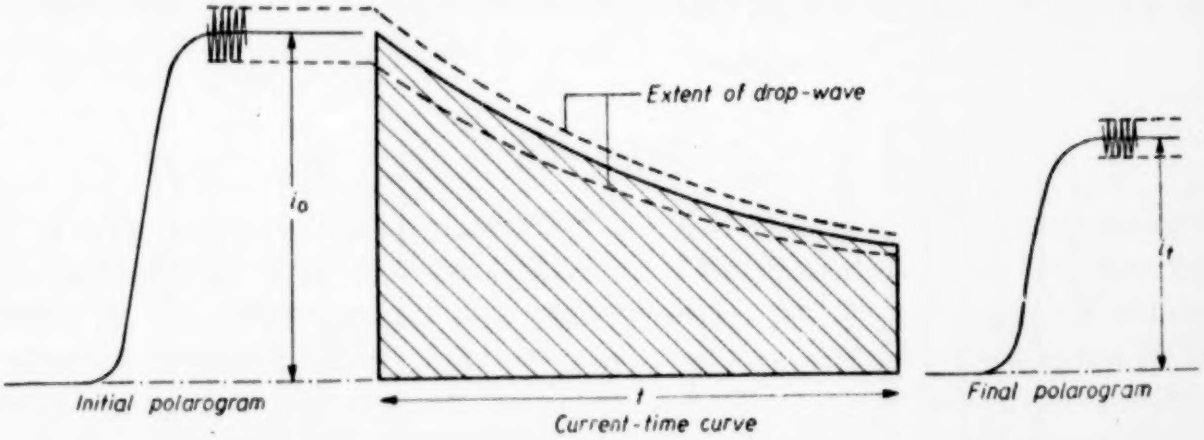


Fig. 2.

on the initial polarogram. A horizontal line was then drawn through this point. The area enclosed by the curve and this line (shaded in Fig. 2) was then cut out and weighed. A standard area of this piece was then also cut out and weighed. As the speed of recording and the absolute sensitivity of the polarograph in micro amps per divison were known it was possible to calculate the number of coulombs passed during the electrolysis.

The weight of the standard area of photographic paper was found to be remarkably constant, in spite of the fact that no attempt was made to standardise the conditions of washing and drying and that different batches of photographic paper (Ilford contact, hard matt) were used. The average weight of 7.5 sq. cm. was 0.145 g and the standard deviation was 0.003 g.

When employing the arithmetic average method the same procedure was used except that the electrolysis was allowed to proceed for only 15-20 minutes. A polarogram was then taken after stirring by passage of hydrogen bubbles. This was repeated at least three times. The results were calculated by means of equation 6. It should be noted that it is necessary to note the time of electrolysis of the solution while the polarogram is being recorded and add this to the time interval already measured.

RESULTS AND DISCUSSION

General

A large number of determinations were carried out using cadmium solutions in order to investigate the effects of variable factors. These factors are listed in Table I below. The results shown in this table for each set of conditions are actually the average of at least four experiments. It was, of course, necessary to carry out separate sets of experiments to obtain results by the arithmetic average and integration methods. Two separate sets of graphical results have

TABLE I

per- ent	Cadmium Concentration (micro g/ml)	HCl Concentration (M)	Volume of solution (ml)	Potential of electrolysis (volts)	Type of anode	Total time of electrolysis (sec)	Value of *n* (average)			
							Arithmetic average	Integration	Graphical	
									Arithmetic average	Integration
1	20	0.1	0.3	0.9	Hg pool	2,700	1.34*	0.84*	0.46*	0.57*
2	100	0.1	0.3	0.9	,,	2,700	2.69*	2.44*	0.30*	0.54*
3	100	0.1	0.3	0.9	Silver	2,700	1.71	1.81	1.17	1.52
4	100	0.1	0.3	1.2	,,	2,700	1.61	1.63	1.64	1.58
5	100	0.1	0.5	1.2	,,	2,700	1.72	1.82	1.45	1.62
6	100	0.1	0.3	0.9	,,	3.360	2.25*	1.83*	2.11*	1.63*
7	500	0.5	0.3	1.2	,,	2,700	1.98*	1.91	1.47*	1.87*
8	500	0.5	0.3	0.9	,,	2,700	1.97*	1.94	1.92	1.85
9	1,000	1.0	0.3	0.9	,,	2,700	2.00	1.87	1.93	1.89

te. All results other than those marked* were obtained with the drawn out "microcapillary" the dropping mercury electrode.

been obtained from these and are given in the last two columns of the table.

Examination of the results in Table I shows that the effect of variation of the concentration of the reacting ion upon the final result is the most important factor. It will be seen that, with the most concentrated solution, good results are obtained by all methods, and that, as the concentration is decreased, the graphical results soon become inaccurate.

It appears from the above that when a high concentration or reacting ion is employed the depletion effect becomes less. This is presumably due to the fact that a much steeper concentration gradient exists. In addition, any errors due to changes in the residual current will be progressively lessened at higher concentrations, although these should not be significant with concentrations greater than $10^{-3}M$ cadmium solutions (112 microg/ml).

Other conclusions drawn from Table I are:

1. The volume of solution electrolysed and the time of electrolysis are not important, except insofar as they affect the time necessary to obtain a reasonable decrease in concentration of the reacting ion. For maximum accuracy the decrease should be as large as possible, but, if the arithmetic average method is to be applied, it should not exceed 50% of the original concentration.
2. The potential of the electrolysis is not critical provided that the value selected ensures that there is no tendency for a less noble ion, if present, to reduce also. However, a potential close to the half-wave potential is to be preferred as reactions may take place at the anode and these will be encourage by an unnecessarily large potential difference between the anode and cathode.
3. The use of a separate anode leads to better results than those obtained with the mercury pool. This is especially the case with deposition reactions, where the amalgam formed at the dropping mercury electrode is transferred directly to the pool, from which re-solution will occur more easily if it is part of the electrical circuit.
4. The use of the micro-capillary already described is not essential, but its use gives smoother current-time curves, which make the graphical method easier to apply.

In addition to the above experiments others using a modified micro-cell (Fig. 1) were carried out. This cell allowed the solution to be mixed and deoxygenated without removing the dropping electrode from the cell. Similar results to those obtained with the first type of cell were obtained. The side tube also enabled a separate mercury anode to be used, but again similar results were obtained with the dilute solutions whilst more concentrated solutions caused polarization of the anode. The use of this cell, which is more difficult to construct and manipulate, was therefore abandoned.

The introduction of a layer of chloroform over the mercury pool was made in an attempt to prevent the re-solution of the deposited ion. This was not very satisfactory and will be discussed in more detail later.

It was shown during the discussion of basic principles that the integration method should give true results regardless of the depletion effect. The results in Table I, however, show that the results obtained with dilute cadmium solutions were consistently low. In spite of this the number of coulombs passed during the electrolysis of the 100 microg/ml cadmium solutions were repeatedly found to be almost exactly one tenth of those passed through the 1000 microg per ml solutions. A micro ammeter in series with the cell confirmed that there was no error in the current measurement. The discrepancy cannot be explained by re-solution from the mercury pool as this would lead to high results.

In order to examine this unexpected feature a series of experiments were carried out using solutions containing 100 microg per ml and 1000 microg per ml respectively of lead. The more concentrated solutions yielded the expected good results, but the results obtained by the integration method with the dilute solutions were consistently high. Once again the ratio of the number of coulombs passed in each case was almost exactly 10 : 1. In spite of very rigid precautions against re-solution (see later) the average values obtained were as shown in Table II.

TABLE II

Concentration of lead microg/ml	Value of *n* Integration Method
1000	2.13
100	3.02

We cannot offer any explanation for this breakdown of the integration method with dilute solutions, but recommend that the error be avoided by the use of concentrated solutions.

Reduction of the chromate ion

The reduction of chromate ion to trivalent chromium in a base electrolyte of sodium hydroxide was selected for investigation as a typical example of an irreversible valency change.

A solution, 200 microg per ml with respect to chromium and 1*M* with respect to sodium hydroxide was prepared and an initial polarogram gave a limiting diffusion current of 25 microamps. A potential of 1.5 applied volts versus the silver anode was selected as a suitable potential for the electrolysis and a volume of 0.3 ml was used throughout. For the integration method the total time of electrolysis was 45 minutes and for the arithmetic method polarograms were recorded every 15 minutes.

The average value for *n* obtained by the arithmetic average method was 5.89, which is almost exactly twice the correct value. A typical set of results for five polarograms is given in Table III.

TABLE III

Polarograms used	n value	Polarograms used	n value	Polarograms used	n value	Polarograms used	n value
1—2	3.05	1—3	4.05	1—4	4.76	1—5	5.6
2—3	5.99	2—4	6.55	2—5	7.67		
3—4	7.18	3—5	8.89				
4—5	11.70						

Average value = 6.54

It will be seen that the result calculated from the first two polarograms is almost exactly correct, but that, as the total time of electrolysis increases the results become more and more inaccurate. Furthermore the result obtained from the fourth and fifth polarograms is worse than that from the first and fifth.

It was concluded that oxidation of the Cr^{+3} ion at the anode was occurring and that results become progressively worse, due to the stirring which preceded the recording of each polarogram. This stirring had the effect of distributing the reduced ion homogeneously through the solution, enabling oxidation at the anode to take place immediately the electrolysis was recommenced.

Results obtained by the integration method were fairly good, presumably due to the fact that the solution is not stirred during this type of determination. In this case, therefore, oxidation can only occur after the reduced form has diffused to the anode. It was shown that increasing the distance of the dropping mercury electrode from the mercury pool had, as would be expected, a beneficial effect on the results.

In order to counteract the oxidation effect the mercury pool was covered with chloroform, but very erratic current-time curves were obtained, due to the combined effects of the slight solubility of the chloroform and its reducibility at the dropping mercury electrode. The use of chloroform was therefore abandoned in favour of trichlorethylene, which was found to be much more satisfactory. Five results obtained by the integration method using trichlorethylene were: 2.72, 2.98, 3.28, 2.95 and 3.09. The average value is therefore 3.01, which is considered to be satisfactory.

The results obtained by the arithmetic average method when trichlorethylene covered the pool were still high, but the average value, 3.92, was considerably better than that obtained with an uncovered pool. The results still showed the same trend as those in Table III, however.

From these results it was concluded that, when the errors due to the depletion effect have been minimised by the use of a concentrated solution, the reoxidation of the reduced ion is the most serious cause of error in the microcoulometric method. If possible, the integration method should always be used for reactions involving a valency change, but if no suitable polarograph is available a limited form of the arithmetic average method must be employed. In this case we recommend that only two polarograms be recorded and that care is taken not to stir the solution until immediately before the second polarogram is recorded.

For all determinations of this type a large reduction in concentration should not be aimed at, as this requires either a long time of electrolysis or a very small volume of solution. Both these factors favour the oxidation of the reduced ion. We have found that a reduction in concentration of 20 per cent. was a satisfactory compromise between maximum accuracy in measurement of the change of concentration and minimum oxidation.

It is, of course, impossible to apply the graphical method to the arithmetic average results, when only two polarograms are recorded, but the method was applied to the curves obtained for the integration method. The values of n obtained were between 2.6 and 2.8, indicating that some depletion was still occurring. Oxidation of the reduced ion would have caused high graphical results and must therefore be almost absent under the conditions adopted for the integration method.

Reversible valency changes

In order to determine to what extent it was possible to prevent oxidation of the reduced ion in the microcoulometric cell, the reversible valency changes:

$$\mathrm{Eu_{III}} \rightarrow \mathrm{Eu_{II}} \text{ and } \mathrm{Cr_{III}} \rightarrow \mathrm{Cr_{II}}$$

were investigated. In spite of the fact that every precaution was taken against oxidation, both at the anode and by atmospheric oxygen, no change in concentration could be detected during the electrolysis. The matter was not pursued, however, in view of the satisfactory nature of the results by the usual methods.

Anodic oxidation

The anodic oxidation of a manganous mannitol complex was chosen for this investigation. The usual log $i/i_d\text{-}i$ graph showed this to be a reversible change involving one electron. As this was an oxidation the galvanometer zero, which was marked on each polarogram, appeared at the top of the step. To carry out the electrolysis the potential was set at a point about 0.2 volts more *positive* (European Convention) than the half-wave potential.

After electrolysis there was no change in step-height, but the galvanometer zero position moved progressively down the step. The electrolysis was usually stopped when this point was located about half way down.

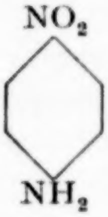
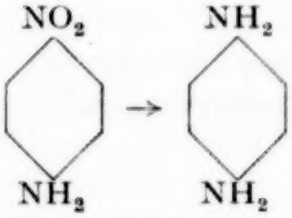
This shift in galvanometer zero should be proportional to the amount of substance which has reacted and a coulometric method for the determination of *n* in reactions of this type should be possible. In this case, however, the results were consistently low and this was shown to be due to the fact that the spontaneous oxidation of the complex (possibly by oxygen dissolved in the solution) is greatly accelerated in the presence of mercury.

As the classical methods of determining *n* values are perfectly satisfactory, no attempt was made to apply this method to other reversible reactions of this type.

Miscellaneous determinations

The coulometric method was applied to the reductions of cobalt and paranitroaniline in order to further test its accuracy. In addition determinations were carried out on the reductions of copper and nickel in $5M$ calcium chloride. In these latter cases the correct *n* values were not definitely known and the microcoulometric method was used to confirm electrode reactions which had been worked out from thermodynamic data[10,11]. The results are given in Table IV.

TABLE IV

Species present	Base electrolyte	Potential of electrolysis	Electrode reaction	Correct n value	n value found Arithmetic average	Integration
Cu(II)	$5M$ $CaCl_2$	—0.375 V	$CuCl^- + 2e^- \rightarrow Cu(Hg) + 2Cl^-$	1	0.85	0.95
Ni(II)	$5M$ $CaCl_2$	—0.6 V	$Ni^{+2} + 2e^- \rightarrow Ni$	2	2.27	2.02
Co(II)	$0.1N$ KCl	—1.35 V	$Co^{+2} + 2e^- \rightarrow Co$	2	2.08	2.07
	$0.1N.$ KCl	—1.20 V		6	6.00	5.70

CONCLUSIONS

Microcoulometric analysis has been shown to be a satisfactory method of determining the number of electrons involved in a unit of reaction at the dropping mercury electrode.

The conditions which should be adopted for the determination of *n* in a completely unknown reaction may be summarised as follows.

1. The integration method should always be used if this is possible. If the type of instrument available precludes this, the arithmetic average method should be employed and when it is obvious from the trend of the results that oxidation at the anode is occurring, only two polarograms should be recorded.

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2. A high concentration of reducible ion should be used.
3. A separate anode should be employed.
4. The mercury pool should be covered with a few drops of trichlorethylene.
5. The potential of the electrolysis should be as close to the half-wave potential as possible, ensuring that the maximum diffusion current is flowing.

Provided that the reaction being studied is not reversible and that the reaction does not give products which will themselves react under the conditions adopted, reliable results should be obtained.

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SUMMARY

A coulometric method of determining the number of electrons taking part in a unit of reaction at the dropping mercury electrode, using only a polarograph and microcell is presented and critically examined. Results obtained with reversible and irreversible depositions and valency changes are discussed and recommendations are made.

RÉSUMÉ

Les auteurs présentent et critiquent une méthode coulométrique pour la détermination du nombre d'électrons intervenant dans les réactions à l'électrode à gouttes de mercure; ils utilisent un polarographe et une microcellule. Les résultats, obtenus par dépôts réversibles et irréversibles et par changements de valence, sont discutés.

ZUSAMMENFASSUNG

Unter Benutzung eines Polarographen und einer Mikrozelle wird eine coulometrische Methode zur Bestimmung der in einer Reaktionseinheit an der tropfenden Quecksilberelektrode teilnemenden Anzahl der Elektronen vorgelegt und kritisch untersucht. Die erhaltenen Resultate mit reversiblen und irreversiblen Niederschlägen und Valenzänderungen werden besprochen und Empfehlungen ausgearbeitet.

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SYMPOSIUM ON ANALYTICAL CHEMISTRY, 1954

President: Professor H. W. Melville, F.R.S.

The Midlands Society for Analytical Chemistry is holding an 8-day Symposium at the University of Birmingham, England, from 25th August to 1st September, 1954. The programme is as follows:

Lectures: The following have consented to contribute:

(a) *Original Papers*

A. A. Smales,
C. Beck,
R. Pribil,
C. Duval,
P. W. West,
F. Burriel,
E. Rancke-Madsen,
A. Ringbom,
H. Flaschka,
F. Lucena,
A. Lacourt,
J. King,
C. L. Wilson,
J. E. B. Randles,
J. Sheridan,
T. B. Smith,
R. Belcher,
K. Gardner,
P. Hersch,
E. Bishop,
H. Thomas,
R. J. P. Williams,
F. Holmes.

(b) *Recent Advances* in selected branches of analysis

Industrial Applications

Iron and Steel	B. Bagshawe,
Non-Ferrous Metals	G. W. C. Milner,
Coal and Coke	R. A. Mott,
Coal Tar	T. A. Vaughan,
Paints and Varnishes	C. Whalley,
Ceramics	H. Bennett,
Foods	D. Dickinson,
Plastics	J. Haslam.

Special Techniques

Inorganic Chromatography	F. H. Pollard,
Mass Spectrometry	J. Robb,
Polarography	W. Cule Davies,
Spectrography	R. L. Mitchell,
Absorptiometry	W. N. Aldridge,
Biochemical Analysis	Garfield Thomas,
Qualitative Analysis	H. Holness,
Ion Exchangers	G. H. Osborn,
The Quantometer	I. G. Slater.

In addition there will be three plenary lectures given by speakers of international repute.

Exhibitions: There will be an exhibition of apparatus, reagents and scientific literature embodying the latest developments in analytical chemistry.

Demonstrations: There will be demonstrations of new techniques.

Library Exhibition: A special exhibition of historical chemical literature, including the Joseph Priestley collection will be on view in the Harding Library.

Visits: A number of visits of scientific and general interest has been arranged to local industrial establishments.

Social Functions: There will be a number of social functions including a symposium dinner and a civic reception.

Ladies Programme: A number of special visits has been arranged for lady visitors.

Registration forms and further information may be obtained on application to the Symposium Secretary.

Symposium Secretary:

Dr. J. W. Robinson,
139 Stourport Road,
Kidderminster,
Worcs.

REDUCTIONS AND OXIDATIONS OF IRON-CYANOGEN COMPOUNDS OF COPPER

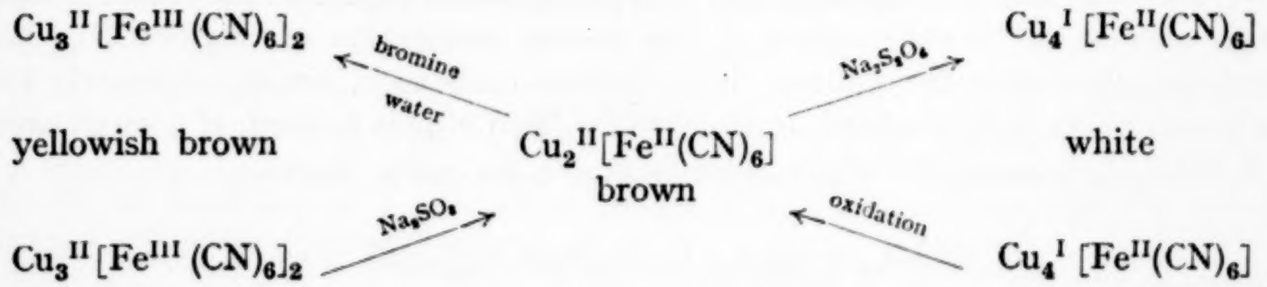
by

MORITZ KOHN*

It was observed more than forty-eight years ago that the blue iron-cyanogen compounds, Prussian blue and Turnbull's blue, are reduced immediately by sodium hyposulfite ($Na_2S_2O_4$) to the white ferrous ferrocyanide $Fe_2[Fe(CN)_6]$[1]. And three years later, TAYLOR recommended, obviously without any knowledge of the publication of the author, the use of $Na_2S_2O_4$ for the reduction of Prussian blue. However, it has been found now that also the brown cupric ferrocyanide is reduced by $Na_2S_2O_4$ to a white substance, undoubtedly a cuprous compound, which can be cuprous ferrocyanide $Cu_4[(Fe(CN)_6]$ or a sodium cuprous ferrocyanide, for instance $Na_2Cu_2[Fe(CN)_6]$.

But the white color turns brownish in a short time if the reaction is carried out in neutral solution. However, the white color is far more stable if a small quantity of sodium carbonate is added to the mixture of copper sulfate and potassium ferrocyanide. The cupric ferrocyanide is easily soluble in disodium tartrate in presence of a small quantity of sodium carbonate and this blue solution formed at ordinary temperature yields after addition of $Na_2S_2O_4$ also the white cuprous ferrocyanide. Bromine water oxidizes cupric ferrocyanide to the yellowish brown cupric ferricyanide. If the white cuprous ferrocyanide is treated with an excess of bromine water cupric ferricyanide is formed because the brown cupric ferrocyanide, which is formed first in this oxidation, is oxidized later to cupric ferricyanide. Sulfites and sulfurous acid also reduce cupric ferricyanide to cupric ferrocyanide only.

The results reported above are summarized as follows:


$Cu_3^{II}[Fe^{III}(CN)_6]_2$
bromine water
$Na_2S_2O_4$
$Cu_4^{I}[Fe^{II}(CN)_6]$
yellowish brown
$Cu_2^{II}[Fe^{II}(CN)_6]$
brown
white
Na_2SO_3
oxidation
$Cu_3^{II}[Fe^{III}(CN)_6]_2$
$Cu_4^{I}[Fe^{II}(CN)_6]$

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References p. 404.

Reduction of cupric ferricyanide to cupric ferrocyanide by sodium sulfite and by sulfurous acid

I. 3 ml 0.1*M* $CuSO_4$ and 2 ml 0.1*M* $K_3[Fe(CN)_6]$ were mixed and 5 ml of a solution containing 0.8 g Na_2SO_3 added whereby the yellowish brown cupric ferricyanide is transformed into brown cupric ferrocyanide. If the mixture is filtered the filtrate contains the excess of sodium sulfite.

II. 5 ml 0.1*M* $CuSO_4$, 1 ml 0.1*M* $K_3[Fe(CN)_6]$, 2.5 ml H_2O were mixed. The addition of 5 ml of a 10% solution of Na_2SO_3 yields cupric ferrocyanide.

III. 1.5 ml 0.1*M* $CuSO_4$, 1 ml 0.1*M* $K_3[Fe(CN)_6]$ and 2.5 ml H_2O were mixed. By addition of 5 ml 0.1*N* HCl and 5 ml of a 10% solution of Na_2SO_3 cupric ferrocyanide is formed.

IV. The same quantities as in III, but instead of 5 ml 0.1*N* HCl an excess of HCl was added. $Cu_2[Fe(CN)_6]$ was formed.

Solubility of cupric ferrocyanide in disodium tartrate in the presence of sodium carbonate

I. 2 ml 0.1*M* $CuSO_4$ and 1 ml 0.1*M* $K_4[Fe(CN)_6]$ were mixed. 5 ml H_2O, 0.1 g Na_2CO_3 and 4 g disodium tartrate were added. A clear blue solution was formed on shaking. The calculated weight of Na_2CO_3 required for the decomposition of the cupric ferrocyanide is 0.0212 g Na_2CO_3 only.

II. 2 ml 0.1*M* $CuSO_4$, 1 ml 0.1*M* $K_4[Fe(CN)_6]$, 11 ml H_2O, 1 ml Na_2CO_3 (containing 0.1 g Na_2CO_3) and 4 g disodium tartrate gave a clear blue solution.

Reduction of cupric ferrocyanide to cuprous ferrocyanide by sodium hyposulfite ($Na_2S_2O_4$)

I. 2 ml 0.1*M* $CuSO_4$, 1 ml 0.1*M* $K_4[Fe(CN)_6]$ and 0.1 g Na_2CO_3 dissolved in 9 ml H_2O were mixed. Although the quantity of sodium carbonate required for the complete decomposition of the precipitated cupric ferrocyanide used in this experiment is only 0.0212 g, the brown precipitate of $Cu_2[Fe(CN)_6]$ does not disappear after the addition of the sodium carbonate. An approximately 10% solution of $Na_2S_2O_4$ is added until white $Cu_4[Fe(CN)_6]$ is formed. If a small excess of $Na_2S_2O_4$ is used the white color is stable for some hours.

II. 2 ml 0.1*M* $CuSO_4$, 1 ml 0.1*M* $K_4[Fe(CN)_6]$ and 9 ml H_2O were mixed. On addition of a solution of $Na_2S_2O_4$ a white precipitate is obtained which changes to a brownish color in a short time.

III. 2 ml 0.1*M* $CuSO_4$, 1.5 ml 0.1*M* $K_4[Fe(CN)_6]$ and 9 ml H_2O were mixed. The addition of a solution of $Na_2S_2O_4$ produced a white precipitate which changed to a brownish color afterwards.

IV. 2 ml 0.1*M* $CuSO_4$, 5 ml 0.1*M* $K_4[Fe(CN)_6]$, and a solution of 0.1 g Na_2CO_3 in 7.5 ml H_2O were mixed. The addition of a solution of $Na_2S_2O_4$ yielded a white precipitate; the white color was stable for some time.

V. 6 ml 0.1*M* $CuSO_4$, 3 ml 0.1*M* $K_4[Fe(CN)_6]$, 12 g disodium tartrate and a solution of 0.3 g Na_2CO_3 in 20 ml H_2O were mixed and shaken afterwards until the disodium tartrate disappeared and a clear blue solution resulted. The addition of $Na_2S_2O_4$ produced a white precipitate stable for some time.

The white precipitates formed in the experiments I, IV and V were filtered and washed with water thoroughly. Afterwards the precipitates were washed off into three beakers. A small excess of bromine water was poured into the beakers, which were kept at room temperature for about half an hour. The mixtures contained in these three beakers were filtered and the excess of bromine was removed by washing. Each of these three products of the oxidation gave the reactions of cupric ferricyanide: The addition of sodium acetate and hydrogen peroxide yielded brown cupric ferrocyanide[3]. The addition of $K_4[Fe(CN)_6]$ also formed cupric ferrocyanide[4], while the filtrate contained $K_3[Fe(CN)_6]$. When ferrous sulfate was dropped into this filtrate, Turnbull's blue was precipitated.

Oxidation of cupric ferrocyanide to cupric ferricyanide by bromine water

26 ml 0.1*M* $CuSO_4$ were precipitated with 12 ml 0.1*M* $K_4[Fe(CN)_6]$. 6 ml bromine water were diluted with 13 ml water. The two solutions were mixed and shaken, the mixture filtered and the precipitate washed with water after 24 hours in order to remove the excess of copper sulfate and of bromine. The precipitate was washed off into a beaker and 20 ml 0.1*M* $K_4[Fe(CN)_6]$ were added. The mixture was stirred and 10 g sodium chloride were added. The cupric ferrocyanide was filtered through the original filter some hours later and the potassium in the filtrate determined with sodium thiosulfate. 11 ml 0.1*N* $Na_2S_2O_3$ were used up. Therefore 91.6% of the ferrocyan was oxidized.

SUMMARY

1. Cupric ferrocyanide is oxidized by bromine water to cupric ferricyanide.
2. Cupric ferrocyanide is soluble in disodium tartrate in presence of a small quantity of sodium carbonate.
3. Cupric ferricyanide is reduced by sodium sulfite or by sulfurous acid to cupric ferrocyanide only.
4. Cupric ferrocyanide is reduced by sodium hyposulfite ($Na_2S_2O_4$) to white cuprous ferrocyanide $Cu_4[Fe(CN)_6]$.

References p. 404.

RÉSUMÉ

1. Le ferrocyanure de cuivre(II) est oxydé par l'eau de brome en ferricyanure de cuivre(II).

2. Le ferrocyanure de cuivre(II) est soluble dans le tartrate disodique, en présence d'un peu de carbonate de sodium.

3. Le ferricyanure de cuivre(II) est réduit par le sulfite de sodium ou par l'acide sulfureux en ferrocyanure de cuivre(II).

4. Le ferrocyanure de cuivre(II) est réduit par l'hyposulfite de sodium ($Na_2S_2O_4$) en ferrocyanure de cuivre(I) blanc, $Cu_4[Fe(CN)_6]$.

ZUSAMMENFASSUNG

1. Kupferferrozyanid wird durch Bromwasser bei gewoehnlicher Temperatur zum Kupferferrizyanid oxydiert.

2. Kupferferrozyanid ist in neutralem Natriumtartarat in Gegenwart geringer Mengen von Natriumkarbonat loeslich.

3. Kupferferrizyanid wird sowohl durch Natriumsulfit als auch durch freie schwefelige Saeure nur bis zum Kupferferrozyanid reduziert.

4. Kupferferrozyanid wird durch hydroschwefligsaures Natrium ($Na_2S_2O_4$) zu weissem Kuproferrozyanid $Cu_4[Fe(CN)_6]$ reduziert.

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IODOMETRIC DETERMINATION OF FERRICYAN IN THE PRESENCE OF COPPER, SILVER, CADMIUM AND ZINC

by

MORITZ KOHN*

For the determination of ferricyan in nickel ferricyanide and in cobalt ferricyanide it was recommended to add potassium ferrocyanide whereby the double decomposition yields nickel ferrocyanide and cobalt ferrocyanide and potassium ferricyanide. The insoluble ferrocyanides can be removed by filtration and the potassium ferricyanide contained in the filtrate can be determined accurately by iodometric titration[1]. However, it seemed necessary to examine whether this procedure could be used in the cases of other insoluble ferricyanides. It will be explained how the same method or modifications of this method can be used in the presence of copper, silver, cadmium and zinc.

Copper

I. 5 ml 0.1*M* $K_3[Fe(CN)_6]$ were precipitated with 7.5 ml 0.1*M* $CuSO_4$. The mixture was shaken and 11 ml 0.1*M* $K_4[Fe(CN)_6]$ were added, whereby brown $Cu_2[Fe(CN)_6]$ was formed. By addition of a solution of 12 g sodium sulfate in 50 ml water the slimy cupric ferrocyanide was coagulated. When the precipitate had settled, it was filtered and washed with 7% sodium sulfate solution. The filtrate used up 4.9 ml 0.1*N* $Na_2S_2O_3$ instead of 5 ml in the titration according to MUELLER AND DIEFENTHAELER[2]. This method was always used in this work.

II. 10 ml 0.1*M* $CuSO_4$ and 10 ml 0.05*M* $K_3[Fe(CN)_6]$ were mixed and 10 ml 0.2*M* $K_4[Fe(CN)_6]$ were added afterwards. The cupric ferrocyanide was coagulated by addition of a solution of 15 g potassium chloride in 30 ml water. The precipitate was filtered, washed with 10% KCl solution. The filtrate used up 8.7 ml of a thiosulfate solution instead of the required volume of 8.62 ml because 17.25 ml of this thiosulfate solution were equivalent to 20 ml 0.05*M* $K_3[Fe(CN)_6]$.

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Silver

The addition of potassium iodide to silver ferricyanide yields quantitatively silver iodide and potassium ferricyanide. A filtration of the AgI is not necessary.

I. 5 ml 0.1*M* $K_3[Fe(CN)_6]$ and 15 ml 0.1*M* $AgNO_3$ were mixed. 2.2 g potassium iodide dissolved in 25 ml water and 2 g zinc sulfate dissolved in 25 ml water were added. The mixture used up 5 ml 0.1*N* sodium thiosulfate.

II. The same quantities and the same procedure as in I. Used up 4.95 ml 0.1*N* sodium thiosulfate.

In III and IV potassium ferrocyanide was used and the mixtures filtered before the titration:

III. 5 ml 0.1*M* $K_3[Fe(CN)_6]$ were precipitated with 15 ml 0.1*N* $AgNO_3$. 15 ml 0.1*M* $K_4[Fe(CN)_6]$ were added, whereby the red-orange silver ferricyanide disappeared because the white silver ferrocyanide and potassium ferricyanide were formed. 40 ml of a 15% solution of sodium sulfate were added. The precipitate settles after some time and can be filtered. It is washed with sodium sulfate solution. The filtrate required 5 ml 0.1*N* $Na_2S_2O_3$.

IV. The same quantities and the same procedure as in III. A solution of 6 g sodium sulfate in 30 ml water was used. The filtrate used up 5.05 ml 0.1*N* $Na_2S_2O_3$.

Cadmium

The determinations which were carried out without a filtration of the cadmium ferrocyanide gave too low results:

I. 5 ml 0.1*M* $K_3[Fe(CN)_6]$ and 8 ml $CdCl_2$ were mixed. 13 ml 0.1*M* $K_4[Fe(CN)_6]$ were added in order to obtain cadmium ferrocyanide and potassium ferricyanide. The mixture was diluted with 30 ml water. 4.5 ml 0.1*N* thiosulfate were used up.

II. In the repetition of I also 4.5 ml 0.1*N* thiosulfate were used up instead of 5 ml 0.1*N* thiosulfate.

In the determinations III and IV the cadmium ferrocyanide was removed by filtration before titration:

III. 5 ml 0.1*M* $K_3[Fe(CN)_6]$ and 8 ml 0.1*M* $CdCl_2$ were mixed. 15 ml 0.1*M* $K_4[Fe(CN)_6]$ were added for the double decomposition. The slimy precipitate was coagulated by addition of a sodium sulfate solution. The cadmium ferrocyanide was filtered and washed with sodium sulfate solution. The filtrate required 5.05 ml 0.1N $Na_2S_2O_3$ solution.

IV. The same quantities as in III. 12 ml 0.1M $K_4[Fe(CN)_6]$ were used and a solution of 5 g sodium sulfate in 20 ml water was added. The filtrate required 4.95 ml 0.1N $Na_2S_2O_3$.

Zinc

The determinations were carried out without filtration of the zinc ferrocyanide.

5 ml 0.1M $K_3[Fe(CN)_6]$, 7 ml 0.1M $ZnSO_4$ were mixed and 15 ml 0.1M $K_4[Fe(CN)_6]$ were added. The mixture was diluted with water. The volume which was titrated was 75 ml. It used up 5.15 ml 0.1M $Na_2S_2O_3$.

SUMMARY

Ferricyan can be determined in the presence of copper, silver and cadmium by addition of potassium ferrocyanide, filtration of the ferrocyanides of copper, silver and cadmium formed in this reaction and titration of the potassium ferricyanide contained in the filtrate. In the case of silver, the ferricyan can also be determined without filtration by addition of potassium iodide and titration of the ferricyanide. In the case of zinc, potassium ferrocyanide is added and without filtration the ferricyanide titrated.

RÉSUMÉ

Les ferricyanures peuvent être dosés en présence de cuivre, argent et cadmium, par addition de ferrocyanure de potassium, filtration des ferrocyanures de cuivre, argent et cadmium formés et titrage du ferricyanure de potassium dans le filtrat. Dans le cas de l'argent, le ferricyanure peut également être déterminé sans filtration, par addition d'iodure de potassium et titrage du ferricyanure. Dans le cas du zinc, on utilise le ferrocyanure de potassium et on titre le ferricyanure sans filtration.

ZUSAMMENFASSUNG

Ferrizyan kann bestimmt werden in Gegenwart von Kupfer, Silber und Kadmium durch Hinzufuegung von Ferrozyankalium, Filtration der in dieser Reaktion gebildeten unloeslichen Ferrozyanide des Kupfers, Silbers und Kadmiums und Titration des im Filtrate enthaltenen Ferrizyankaliums. Im Falle des Silbers genuegt es auch, nur Jodkalium zuzusetzen und ohne eine Filtration das Kaliumferrizyanid zu titrieren. Im Falle des Zinks wird Kaliumferrozyanid zugesetzt und ebenfalls ohne eine Filtration titriert.

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SODIUM META-VANADATE AS VOLUMETRIC REAGENT
I. IODINE MONOCHLORIDE METHOD

by

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SIROKOMSKI AND KLIMENKOV[1] used ammonium meta-vanadate for the volumetric estimation of iron, molybdenum and copper using phenanthranilic acid as an indicator.

GOPALA RAO and co-workers[2] have shown that sodium vanadate has special advantages over potassium permanganate and dichromate as a volumetric reagent. It can be used for the estimation of ferrous salts in the presence of oxalic acid, citric acid, alcohols and phenols where potassium permanganate, potassium dichromate and even ceric sulphate give too high results. They have used sodium vanadate for the volumetric estimation of ferrocyanide alone and in the presence of hydrochloric acid and oxalic acid, hydroquinone in the presence of some phenolic compounds, uranium, tartaric acid, indigo and indigo carmine, using diphenylbenzidine as an internal indicator.

In the present investigation sodium meta-vanadate has been used as a volumetric reagent for the determination of potassium iodide, sodium arsenite, mercurous chloride, potassium thiocyanate, sodium sulphite, sodium bisulphite, sodium thiosulphate, ferrous sulphate and hydrazine sulphate. In the presence of hydrochloric acid these substances react with sodium meta-vanadate in accordance with the equations:

$$
\begin{aligned}
&I^- + 2\,VO_3^- + 8\,H^+ = I^+ + 2\,VO^{+2} + 4\,H_2O\\
&AsO_3^{-3} + 2\,VO_3^- + 6\,H^+ = AsO_4^{-3} + 2\,VO^{+2} + 3\,H_2O\\
&Hg_2^{+2} + 2\,VO_3^- + 8\,H^+ = 2\,Hg^{+2} + 2\,VO^{+2} + 4\,H_2O\\
&CNS^- + 6\,VO_3^- + 16\,H^+ = CN^- + SO_4^{-2} + 6\,VO^{+2} + 8\,H_2O\\
&SO_3^{-2} + 2\,VO_3^- + 6\,H^+ = SO_4^{-2} + 2\,VO^{+2} + 3\,H_2O\\
&HSO_3^- + 2\,VO_3^- + 5\,H^+ = SO_4^{-2} + 2\,VO^{+2} + 3\,H_2O\\
&S_2O_3^{-2} + 8\,VO_3^- + 22\,H^+ = 2\,SO_4^{-2} + 8\,VO^{+2} + 11\,H_2O\\
&Fe^{+2} + VO_3^- + 4\,H^+ = Fe^{+3} + VO^{+2} + 2\,H_2O\\
&N_2H_4 + 4\,VO_3^- + 12\,H^+ = N_2 + 4\,VO^{+2} + 8\,H_2O
\end{aligned}
$$

References p. 412.

EXPERIMENTAL

A known amount of each substance was taken in a conical flask and about 25 ml of water, 30 ml of concentrated hydrochloric acid, 5 ml of $0.02M$ iodine monochloride and 5 ml of chloroform were added to it. The mixture was cooled to room temperature and titrated against standard sodium meta-vanadate solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale green and the chloroform layer acquired purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the meta-vanadate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The meta-vanadate was then added dropwise, with shaking after the addition of each drop, until the chloroform layer became light pale yellow. The end-point was very sharp.

In these titrations, normality of the solution with respect to hydrochloric acid was kept between $7N$ to $7.5N$ even at the end-point by the addition of more acid. Several titrations were performed in each case. From the volume of sodium meta-vanadate used, corresponding to the end-point in each titration, the amount of each substance was calculated. The results are given in the following tables:

TABLE I

POTASSIUM IODIDE

KI taken g	$N/10$ $NaVO_3$ used ml	KI found g
0.0830	10.00	0.0830
0.1494	18.00	0.1494
0.1992	24.05	0.1996
0.2490	30.10	0.2498
0.2656	32.10	0.2664

TABLE II

SODIUM ARSENITE

Na_3AsO_3 taken g	$N/10$ $NaVO_3$ used ml	Na_3AsO_3 found g
0.0672	7.00	0.0672
0.1056	11.00	0.1056
0.1439	15.02	0.1441
0.1919	20.05	0.1924
0.2207	23.07	0.2214

TABLE III

MERCUROUS CHLORIDE

Hg_2Cl_2 taken g	$N/10$ $NaVO_3$ used ml	Hg_2Cl_2 found g
0.1652	7.00	0.1652
0.2361	10.00	0.2361
0.3541	15.00	0.3541
0.4721	20.00	0.4721
0.5902	25.05	0.5914

TABLE IV

POTASSIUM THIOCYANATE

KCNS taken g	$N/10$ $NaVO_3$ used ml	KCNS found g
0.0079	4.90	0.0079
0.0158	9.80	0.0159
0.0237	14.75	0.0238
0.0317	19.70	0.0319
0.0364	22.60	0.0365

TABLE V

SODIUM SULPHITE

Na_2SO_3 taken g	$N/10$ $NaVO_3$ used ml	Na_2SO_3 found g
0.0504	8.00	0.0504
0.0756	12.00	0.0756
0.1008	15.95	0.1005
0.1260	20.00	0.1260
0.1575	25.00	0.1575

TABLE VI

SODIUM BISULPHITE

$NaHSO_3$ taken g	$N/10$ $NaVO_3$ used ml	$NaHSO_3$ found g
0.0520	10.00	0.0520
0.0676	13.00	0.0676
0.0884	17.03	0.0886
0.1040	20.00	0.1040
0.1248	24.00	0.1248

TABLE VII

SODIUM THIOSULPHATE

$Na_2S_2O_3.5H_2O$ taken g	$N/10$ $NaVO_3$ used ml	$Na_2S_2O_3.5H_2O$ found g
0.0217	7.00	0.0217
0.0372	12.00	0.0372
0.0527	17.10	0.0530
0.0620	20.00	0.0620
0.0713	23.05	0.0715

TABLE VIII

FERROUS SULPHATE

$FeSO_4.7H_2O$ taken g	$N/10$ $NaVO_3$ used ml	$FeSO_4.7H_2O$ found g
0.2502	8.95	0.2488
0.3614	13.00	0.3614
0.4448	15.95	0.4434
0.5560	20.00	0.5560
0.6950	25.00	0.6950

TABLE IX

HYDRAZINE SULPHATE

$N_2H_4.H_2SO_4$ taken g	$N/10$ $NaVO_3$ used ml	$N_2H_4.H_2SO_4$ found g
0.0325	10.00	0.0325
0.0488	15.00	0.0488
0.0650	20.05	0.0652
0.0715	22.00	0.0715
0.0812	25.02	0.0813

From the above tables it is evident that potassium iodide, sodium arsenite, mercurous chloride, potassium thiocyanate, sodium sulphite, sodium bisulphite, sodium thiosulphate, ferrous sulphate and hydrazine sulphate can be determined quantitatively by the iodine monochloride method, using sodium meta-vanadate as volumetric reagent.

SUMMARY

Sodium meta-vanadate has been used as an oxidising agent in hydrochloric acid medium for the volumetric estimations of potassium iodide, sodium arsenite, mercurous chloride, potassium thiocyanate, sodium sulphite, sodium bisulphite, sodium thiosulphate, ferrous sulphate and hydrazine sulphate, using iodine mono-

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chloride as a catalyst and preoxidiser. Chloroform is used as an indicator. It is coloured pink due to the liberation of iodine during the titration and becomes light pale yellow at the end-point due to the formation of iodine monochloride.

RÉSUMÉ

Le métavanadate de sodium est utilisé comme oxydant, en solution chlorhydrique, pour les dosages volumétriques de l'iodure de potassium, de l'arsénite de sodium, du chlorure de mercure (I), du thiocyanate de potassium, des sulfite, bisulfite et thiosulfate de sodium, du sulfate de fer (II) et du sulfate d'hydrazine; on utilise le monochlorure d'iode comme catalyseur et ,,préoxydant''. Le chloroforme, employé comme indicateur, est coloré en violet par l'iode pendant la titration et devient jaune pâle au point final en raison de la formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Zur volumetrischen Bestimmung von Kaliumjodid, Natriumarsenit, Mercurochlorid, Kaliumrhodanid, Natriumsulfit, Natriumbisulfit, Natriumthiosulfat, Ferrosulfat und Hydrazinsulfat wurde Natriummetavanadat in salzsaurem Medium als Oxydationsmittel und Jodmonochlorid als Katalysator und Voroxydationsmittel benützt. Chloroform wird als Indikator verwendet. Es wird von dem freigesetzten Jod während der Titration rosa und am Endpunkt von dem gebildeten Jodmonochlorid schwach hellgelb gefärbt.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURES OF SULFONAMIDES VIII

by

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VI. *Gravimetric and titrimetric determinations of the -SO_2NH-group**

The acid properties of the aromatic -SO_2NH-group of the sulfonamides can in several ways be used for their quantitative determination:

A. The compounds are dissolved in a known amount of 0.1*N* NaOH and the excess back-titrated with acid and a suitable indicator.

B. The compounds are dissolved in *n*-butylamine and titrated with sodium methoxide.

C. The compounds are precipitated as silver salts, the precipitate is filtered and the excess silver nitrate in the filtrate is determined. The silver content of the precipitate can also be determined.

A. It is of great importance for the acidimetric titration that aqueous solutions of the sodium salts of the various sulfonamides do not show the same alkalinity when the concentrations are equal. This means that the acidity of the -SO_2NH-group is different in the various compounds, or, in terms of the Brönsted-theory, that this group has different pK_{H_2O}'s. This makes it questionable as to whether the acidimetric titration of a mixture of sulfonamides is possible at all. Therefore we must first consider the proper alkalinity of solutions of the various sodium salts and the effect of the choice of an unsuitable indicator in their acidimetric titrations.

In Table XVIII some pH-values of solutions of sodium sulfonamides are listed. They are established with the aid of a Beckmann-pH-meter. Sulfaguanidine is not included, since it does not contain a -SO_2NH-group, and is thus insoluble in alkali.

A number of acidimetric titrations of sulfonamides have been mentioned in the literature: Lapière *et al.*[2,3,24], Van Arkel and Wuiste[99]. The influence of the use of an unsuitable indicator has been investigated by Lapière[2]; his results are summarized in Table XIX.

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* See schedule in *Anal. Chim. Acta*, 9 (1953) 142.

TABLE XVIII

Compound	Conc. of aq. sol. of sodium salt	pH
Elkosin	1%	8.9
Sulfadiazine	1%	8.7
Sulfamerazine	1%	9.0
Sulfamezathine	1%	9.2
Irgafen	1%	7.2
Irgamid	1%	7.7
Sulfathiazole	1%	9.2
Sulfamethylthiazole	1%	9.6
Succinylsulfathiazole	1%*	8.1
Sulfanilamide	1%	10.3
Sulfacetamide	1%	8.0
Septazine	sodium salt almost	insoluble
Sulfapyridine	1%	10.1

* di-sodium salt.

It may be concluded that in the acidimetric titration good results are only obtained if an indicator is used whose pH-range coincides with the pH-value of the sodium sulfonamide solution. Fundamentally, the titration can therefore only be applied to mixtures if each separate component-sulfonamide could be titrated with the same indicator. From the data of Table XIX it appears, however, that the errors involved in the choice of an unsuitable indicator are not so large as to render the titration worthless. This determines the applicability of the method to mixtures.

TABLE XIX

Compound	pH (Table XVIII)	Indicator	Results (%)
Sulfacetamide	8.0	phenolphthalein	102.0-102.7
		methyl red	98.0-98.5
		cresol red	99.5-100.1
Sulfapyridine	10.1	thymolphthalein	97.0-97.5
		tropaeoline O	99.5-100.0

In our experiments a weighed quantity of the material to be analyzed was always dissolved in a measured quantity of 0.1*N* NaOH. Water was then added to obtain a concentration of about 2%. Next, half the volume of ethyl alcohol (96%) (previously neutralized to the indicator that is to be used) is added, and the solution titrated with 0.1*N* HCl.

In Table XX our results of the analysis of pure sulfonamides are summarized. We must notice that the pH-ranges indicated holds for pure alcoholic solutions of the indicators, while in our investigations we used a solvent containing 30% of ethyl alcohol and 70% of water. In this solvent both limits of a pH-range tend to lower. On the other hand, the pH-values of aqueous sodium salt solutions as indicated in Table XVIII are somewhat higher in the dilute alcoholic solution used here. This shift in pH-value amounts at most to one unit.

TABLE XX

Compound	Indicator	pH-range	Recovery %
Elkosin	phenolphthalein	8.2-10.0	99.8-100.2
Sulfadiazine	phenolphthalein	8.2-10.0	99.9-100.2
Sulfamerazine	thymolphthalein	9.3-10.5	99.6-99.9
Sulfamezathine	thymolphthalein	9.3-10.5	99.7-99.8
Irgafen	cresol red	7.2- 8.8	99.9-100.3
Irgamid	cresol red	7.2- 8.8	100.2-100.3
Sulfathiazole	thymolphthalein	9.3-10.5	100.0-100.2
Sulfamethylthiazole	thymolphthalein	9.3-10.5	99.5- 99.7
Succinylsulfathiazole	phenol red	6.8- 8.4	99.8-100.0
Sulfacetamide	cresol red	7.2- 8.8	99.9-100.4

Irgafen may cause some trouble on account of the slight solubility of its sodium-salt in dilute aqueous sodium hydroxide. Precipitation may be avoided by dissolving the compound in neutralized acetone and adding the sodium hydroxide to this solution.

Irgamid may first be dissolved in alcohol, and sodium hydroxide and water added next. The fine particles of this compound (and of all other sulfonamides investigated) are only difficultly moistened. We found it attractive, therefore, to stir the compounds with some alcohol to moisten them completely previous to the addition of the alkali.

The titration of sulfapyridine and sulfanilamide seemed impossible to us, since the end-point was very indistinctly visible with the indicator used (tropaeoline O, pH-range 11.1-12.7).

In Table XXI a few examples are given of the application to mixtures using thymolphthalein as indicator. Data indicate that results of practical value are obtained in spite of the use of an indicator that is unsuitable for one of the compounds present. Mixtures were prepared in the way described in our previous communication.

We here refer to our sixth paper in this series, where we discussed the principle of calculating the composition of a mixture from determinations of certain elements or groups that are common to all compounds present.

B. The acidic properties of the -SO_2NH-group may be sufficiently enhanced by using basic organic solvents to permit direct titration with a strong base. This principle has been adopted by FRITZ AND LISICKI[100] and FRITZ AND KEEN[101],

TABLE XXI

Compound	Quantity in g	Found %
Sulfamerazine	0.7324	99.7
Sulfamezathine	0.6336	99.7
Sulfathiazole	0.6207	
Sulfamerazine	0.5361	101.0
Sulfamezathine	0.6163	101.1
Irgamid	0.1379	
Sulfamerazine	0.6174	101.8
Sulfamezathine	0.4407	101.9
Irgamid	0.9571	

who used *n*-butylamine and dimethylformamide as solvents and sodium methoxide as titrant. The former solvent enhances the acid strength of the -SO_2NH-group more than the latter. Sulfanilamide, for example, could not be titrated in dimethylformamide solution, but gave good results in butylamine[101]. In our investigations we therefore used the latter as a solvent, and azo-violet (*p*-nitrobenzeneazoresorcinol, saturated solution in benzene) as an indicator. The 0.1*N* solution of sodium methoxide was prepared as described by FRITZ AND LISICKI[100] and standardized against benzoic acid (A.R.).

Procedure. 200 to 400 mg of the compound or mixture to be titrated is placed in an erlenmeyer flask and dissolved in 30 to 40 ml of *n*-butylamine, which shortly before use is exactly neutralized with sodium methoxide on the azo-violet indicator. The solution is then titrated with sodium methoxide.

The sodium methoxide solution is fairly sensitive to carbon dioxide, and therefore must be protected from air while stored. The solution being titrated may conveniently be protected from carbon dioxide by fitting the Erlenmeyer flask with a little rubber cap provided with a hole to admit the buret tip. The bubbling through of CO_2-free nitrogen is, of course, more suitable, but also more cumbersome.

The titration of simple sulfonamides in all cases gave very good results, percentages found varying from 99.5 to 100.5. Sulfaguanidine cannot be titrated, of course, a -SO_2NH-group being absent in this compound.

Some examples of the application to mixtures are given in Table XXII. The preparation of the mixtures is indicated in our previous communication.

We may conclude that the titration of mixtures of sulfonamides using a basic organic solvent gives very good results. From a theoretical point of view it must

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even be called more reliable and satisfactory than the method discussed under A, since there we are often forced to use an indicator unsuitable for some constituents of the mixture.

TABLE XXII

Compound	Quantity in g	Found %
Sulfamerazine Sulfamezathine Sulfathiazole	0.7324 0.6336 0.6207	99.5 99.9
Sulfadiazine Sulfamerazine Sulfamezathine	0.5397 0.4812 0.6142	100.4 99.8
Sulfanilamide Sulfathiazole Sulfapyridine	0.7504 0.6930 0.5237	100.2 100.6

C. One condition for the determination of sulfonamides via their silver salts is the "complete" insolubility of these salts in the medium employed. This condition, however, is not always fulfilled, and it will be seen below that the method lacks general applicability.

Quantitative determinations using the silver salts are reported from: sulfadiazine[51], sulfamerazine[51], sulfamezathine[51], sulfapyridine[2], sulfathiazole[2], sulfamethylthiazole[102], and elkosin[103].

In investigating the determination of other sulfonamides by way of their silver salts we used the procedure of LAPIÈRE[2]. 0.2-0.3 g of the compound was dissolved in as small a quantity of 0.1*N* sodium hydroxide as possible (faint blue colour of thymolphthalein of which one drop was added). After diluting with 50 ml of water one drop of 0.1*N* H_2SO_4 was added (indicator colourless). Next the silver salt was precipitated by adding 25 ml of 0.1*N* silver nitrate solution. The precipitate was filtered through a double filter paper and thoroughly washed with pure water. The filtrate was acidified with nitric acid and the excess silver nitrate titrated with ammonium rhodanide and ferri-ammonium sulfate.

Precipitating and filtering must be carried out in the dark.

The avoidance of nitric acid in the solution and the wash water forms the only difference between this determination and the classical Volhard-titration. This is caused by the solubility of the silver salts in nitric acid. The liquid must therefore always be neutral to slightly alkaline.

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A determination of the silver-content of the precipitate can be performed according to Stainier and Lapière[3], but was not carried out by us.

We obtained the following results. Soluseptazine and irgafen yielded only a slight precipitation with silver nitrate, and a quantitative determination according to the method described proved impossible therefore.

Septazine turned out to be so slightly soluble in alkali and in acid that a sufficiently concentrated clear solution could not be obtained.

The results with the other compounds are summarized in Table XXIII.

TABLE XXIII

Compound	Found %		
Sulfacetamide	93.8	94.9	95.7
Sulfanilamide	81.5	82.1	81.8
Irgamid	99.6	99.9	99.4
Sulfamethylthiazole	99.3	99.6	99.5
Elkosin	99.4	99.7	99.7
Succinylsulfathiazole	98.7	99.3	99.0

Summarizing our results and those from the literature we can say that the following sulfonamides can be determined following the procedure given:

sulfadiazine
sulfamerazine
sulfamezathine
elkosin
sulfathiazole
sulfamethylthiazole
sulfapyridine
irgamid
succinylsulfathiazole

whereas the determination cannot be carried out with

soluseptazine
irgafen
septazine
sulfaguanidine
sulfanilamide
sulfacetamide

The argentometric determination of a mixture of sulfonamides is thus *only* possible if compounds belonging to the last-mentioned group are *completely* absent (with the exception of sulfaguanidine, which is insoluble in sodium hydroxide and thus can be removed by filtering).

A few examples are given in Table XXIV.

D. The insolubility of the mercury salts has in a few cases been used for quantitative determination[2,104,105], but was not further studied by us.

VII. *Gravimetric and titrimetric determinations of the aromatic -NH_2-group*

The most important determination of this group, namely the nitrite-titration, has already been discussed in detail by us (this journal 9 (1953) 314). Another determination, based on the basic properties of the group, is known, but has not yet found important application.

TABLE XXIV

Compound	Quantity in g	Found %
Sulfadiazine	0.5328	100.3
Sulfamerazine	0.5713	100.0
Sulfamezathine	0.6044	
Sulfathiazole	0.7160	99.6
Sulfadiazine	0.6989	100.1
Sulfathiazole	0.6752	99.6
Elkosin	0.7086	99.8
Irgamid	0.7241	99.4
Sulfamethylthiazole	0.7116	99.5

In this method the compounds are dissolved in glacial acetic acid and titrated with a 0.1*N* solution of perchloric acid in acetic acid. The end-point can be detected potentiometrically or by means of an indicator (crystal violet[106], α-naphthol-benzein[107]). However, results found by various investigators have not been concordant. TOMIČEK[107] reported successful titrations of sulfanilamide, sulfamethylthiazole and sulfapyridine, while VAN ARKEL AND KROONENBERG[108] could not detect the end-point (neither potentiometrically nor with an indicator) in the titration of sulfathiazole, sulfapyridine, sulfadiazine, sulfamerazine, sulfamezathine, sulfaguanidine, succinylsulfathiazole and sulfacetamide.

VIII. *The determination of the amidic -NH-R-groups*

Upon inspecting the formulae of the various sulfonamides (*cf.* Table I, *Anal. Chim. Acta,* 7 (1952) 43), it can be seen that hydrolysis of the -SO_2NH-R-groups always will result in the formation of sulfanilic acid (exception: septazine) and NH_2R or NH_3 and acid (the latter in irgamid, irgafen and sulfacetamide). It may now be asked whether determination of these various products is possible or not. As we will discuss briefly here, great practical difficulties have up to the present rendered the determination of mixtures in this way nearly impossible.

a) Gravimetrical or titrimetrical determinations of one of the compounds without previous isolation is impossible owing to interferences of the other compounds present.

b) The properties of sulfanilic acid causes steam distillation to be the only practical way of isolating the products of the hydrolysis*. Here we must distin-

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* The use of ion-exchange columns might be another means, but so far its application to this problem has not been reported.

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guish the alkaline compounds (ammonia, aminopyridine, aminothiazole, etc.) from the acidic ones (acetic acid, dimethylbenzoic acid). The former are steam-distilled from an alkaline solution, the latter from an acidic one.

1. The most important compounds in the first group are the heterocyclic amines. In a series of experiments we hydrolysed various pure sulfonamides by refluxing 200 mg with 7 ml of 70% sulfuric acid (Schuleck and Boldizsar[85]). After adding sufficient 20% sodium hydroxide solution (1 ml excess) the liquid was steam-distilled, the receiver containing 50 ml of $0.1N$ hydrochloric acid. Distillation was continued till the volume of the liquid in the receiver had attained 500 ml. The excess acid was then back-titrated, using methyl red as the indicator.

It turned out that the dimethylaminopyrimidines from sulfamezathine and elkosin could successfully be determined in this way, as well as methylaminothiazole from sulfamethylthiazole and ammonia from irgamid and irgafen. But aminopyrimidine, methylaminopyrimidine and aminothiazole (from sulfadiazine, sulfamerazine and sulfathiazole resp.) did not show a distinct end-point. The same proved to be true when the titration was carried out potentiometrically.

2. The various acid compounds present yet more difficulties. Acetic acid from sulfacetamide could nearly quantitatively be recovered (98.7%, 99.2%) after addition to the solution to be steam-distilled of sufficient potassium permanganate to destroy interfering sulfur dioxide (which may be present owing to the oxidizing properties of sulfuric acid).

Dimethylacrylic acid from irgamid is nearly completely destroyed by boiling with sulfuric acid, partially yielding *iso*butene and carbon dioxide, partially products of polymerization and addition.

Dimethylbenzoic acid from irgafen is not sufficiently volatile with steam to permit a quantitative distillation in a reasonable time. Recoveries were obtained of 80-90%.

Succinic acid (from succinylsulfathiazole) is yet less volatile with steam than dimethylbenzoic acid.

SUMMARY

The quantitative analysis of mixtures of sulfonamides by means of the acidimetric and argentometric titration of the -SO$_2$NH-group and by means of various determinations of the aromatic -NH$_2$-group and the amidic -NH-R-group is discussed. The acidimetric titration of the -SO$_2$NH-group (in two different performances) proved to be well suited. The argentometric titration is acceptable, though less universally applicable.

RÉSUMÉ

L'analyse quantitative des mélanges de sulfamidés au moyen de la titration acidimétrique et argentométrique du groupe -SO$_2$NH- et au moyen de plusieurs déterminations du groupe aromatique -NH$_2$ et amidique -NH-R est discutée. La titration acidimétrique du groupe -SO$_2$NH- (par deux méthodes différentes) est satisfaisante. La titration argentométrique peut être utilisée, mais elle est moins universellement applicable.

ZUSAMMENFASSUNG

Die quantitative Analyse von Sulfonamidgemengen mittels die azidimetrische und argentometrische Titration der -SO_2NH-Gruppe und mittels verschiedene Bestimmungen der aromatischen -NH_2-Gruppe und amidischen -NH-R-Gruppe wird beschrieben. Die azidimetrische Titration der -SO_2NH-Gruppe (in zwei verschiedenen Ausführungen) zeigte sich geeignet. Die argentometrische Titration kann benützt werden, ist aber nicht universell anwendbar.

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THE ANALYSIS OF COMBUSTION PRODUCTS

I. SOME IMPROVEMENTS IN THE METHODS OF ANALYSIS OF PEROXIDES

by

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In spite of the large volume of publications on the analysis of peroxides, no single procedure has become generally accepted as the most suitable, and modifications are frequently reported. It is therefore relevant to collect together the improvements which have been made in these laboratories in the course of several years of research on combustion problems. As a result of these investigations, three methods are now in general use for quantitative estimations. A modification of the stannous chloride reduction is used for quantities of organic peroxides large enough to be titrated. For very small amounts of organic peroxides and of hydrogen peroxide, it is shown that the thiocyanate reagent can be used with accuracy, while the titanous sulphate method is the simplest one suitable for estimating traces of hydrogen peroxide.

It must be appreciated that when aldehydes are present in a mixture with alkyl hydroperoxides, the formation of hydroxyperoxides occurs to an extent which depends on the pH, the concentration and the time of reaction. The complications introduced by the formation of these hydroxyperoxides will be discussed in a later communication in this series.

Stannous chloride method. The stannous chloride method has recently been improved considerably by BARNARD AND HARGRAVE [1], who showed that it could be made into one of the most accurate ways of estimating organic peroxides, when titratable quantities are available. They carried out the reduction in acetic acid as a solvent, the reaction requiring one hour. In studies of the decomposition of organic peroxides in flow systems (EGERTON AND RUDRAKANCHANA[2]), however, it was found that acetic acid was not sufficiently effective in trapping hydrogen peroxide and *t*-butyl hydroperoxide. The traps were therefore filled with sodium hydroxide solution which converted the peroxides into their sodium salts, without loss of peroxide. Stannous chloride was added, and the reduction in alkaline medium now took place in only a few minutes instead of an hour.

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The reagent is made up by dissolving 11.3 g of AnalaR stannous chloride in a solution of 75 ml conc. hydrochloric acid diluted with 925 ml of air-free water. The solution is kept in an automatic burette under an atmosphere of hydrogen. The procedure is as follows:

About one milli-equivalent of peroxide is weighed and dissolved in 20 ml of 30% sodium hydroxide in a long necked 250 ml flask. The flask is evacuated to *ca.* 10 mm pressure for 5 minutes and filled with nitrogen. Standard stannous chloride (15 ml of 0.1N) is now added, and the flask again pumped out and filled with nitrogen, the latter process being repeated twice. After standing for three minutes, the contents of the flask are acidified with 25 ml of 7.5N sulphuric acid. The regenerated stannous chloride is immediately titrated with standard 0.05N iodine solution in a stream of nitrogen. A blank reaction, without peroxide, is also carried out.

The method has been tested by comparing the results obtained with those given by the BARNARD AND HARGRAVE procedure.

TABLE I

Sample	Peroxide	Method % by B. and H.	Present	Difference
A	*iso*-PrOOH	64.0	63.0	−1.0
B	,,	37.2	38.3	+1.1
C	*tert.*-BuOOH	64.5	64.3	−0.2
	,,	65.2	65.8	+0.6
	,,	66.0	66.1	+0.1

The modification of the method does not appear to lead to results significantly different from those obtained with the original technique. Clearly, hydroperoxides and dialkyl peroxides may be distinguished, if the need arises, by estimating the former by the present method, and the others by following the alkaline trap with an acetic acid one and applying the BARNARD AND HARGRAVE technique to the peroxides trapped in the latter.

Ferrous thiocyanate method. Although some workers in the past have found the method very successful (*e.g.* EGERTON, SMITH AND UBBELOHDE[3]) many authors have experienced difficulties. The reason for the latter have been worked out by KOLTHOFF AND MEDALIA[4] in an extensive review of the mechanisms involved. A general difficulty has always been the instability of the colour. This was found to deepen rapidly, owing to the action of atmospheric oxygen, and the application of spectrophotometric techniques was rendered difficult by this. The usual method recommended in the literature for the decolourization of the reagent itself was to add iron wire to the acidified reagent. This evolved hydrogen which kept the reagent in a reducing atmosphere. However, this was not very satisfactory. During the present work, it was found that the red colour could be removed by extraction with amyl alcohol. The colourless solution then reacted with hydrogen peroxide or with organic peroxide to give a red colour which was quite stable. The intensity of the colour could therefore be measured with a Unicam SP 500 spectrophotometer in 10 mm cells. The optical density was found to be exactly proportional to the original concentration of peroxide, whether this was hydrogen-, ethyl- or *tert.*-butyl-hydroperoxide, or diethyl peroxide. It has not yet been decided whether the stabilization of the colour is due to the formation of a protective film of amyl alcohol, or whether the alcohol reduces the solubility of oxygen or whether it acts as a chain breaker in the oxidation by atmospheric oxygen.

A number of experiments have been carried out to determine the most suitable operating conditions. The reagent is now made up by dissolving 5 g AnalaR ammonium thiocyanate and 5 g AnalaR ferrous sulphate in 100 ml of water containing 1 ml of conc. sulphuric acid. The solution is freed of the red colour by shaking with amyl alcohol. The analyses are carried out by adding to 3 ml of test solution, 1 ml of reagent, which has been shown to be sufficient to develop the colour fully. The colour appears to reach the maximum intensity instantaneously, and is compared on the spectrophotometer against a solution of 1 ml of reagent in 3 ml water. The optical density remains sensibly constant for at least two hours. The concentration is then read off from a calibration curve constructed by the use of standard peroxide solutions.

The spectrum of the hydrogen peroxide - reagent mixture was measured for several concentrations of hydrogen peroxide. It was found that the maximum absorption was always at 4500 A, as shown in Fig. 1, and this wavelength was adopted for further work.

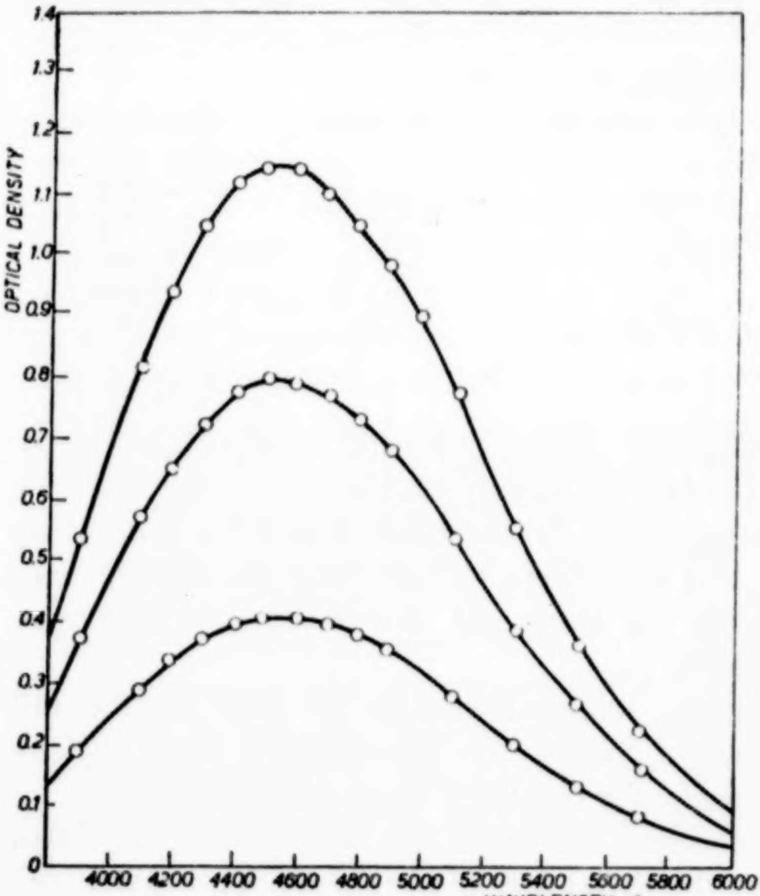

Fig. 1

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The data obtained showed that Beer's Law is accurately obeyed, as shown in Fig. 2.

When identical samples of hydrogen peroxide were analyzed with the same batch of reagent, the standard deviation was ±0.006, which is equivalent to an error of 0.5%. The lowest concentration of hydrogen peroxide which could be estimated was about 0.03 micrograms per ml.

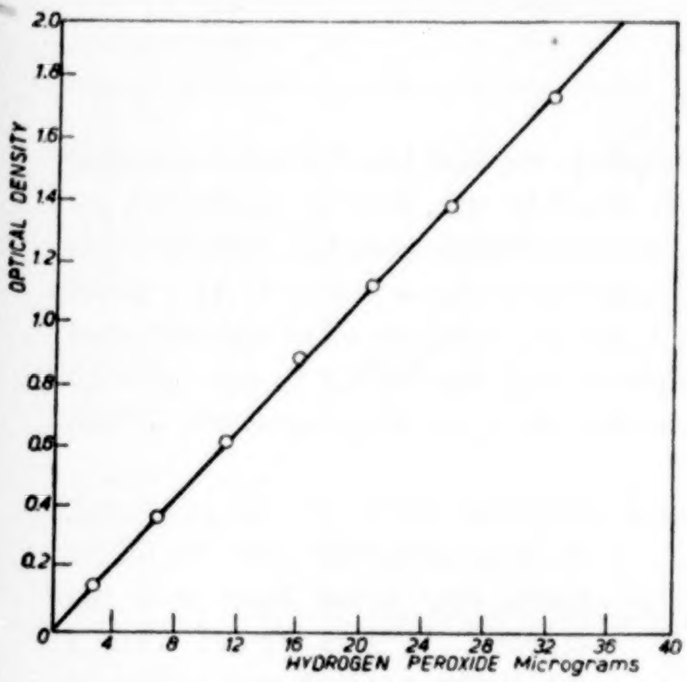

Fig. 2

The method can be applied to the analysis of very dilute solutions of organic peroxides, since it has been shown that the intensity of colour produced is proportional to the concentration of the organic peroxide. Typical results obtained with ethyl hydroperoxide and with ter-butyl hydroperoxide are illustrated in the following graphs, Figs. 3 and 4.

The lower limit of detection is similar to that of hydrogen peroxide. Diethyl peroxide has been tested with a Klett colorimeter. The ratios determined by this method are compared with the theoretical ratios in Table II.

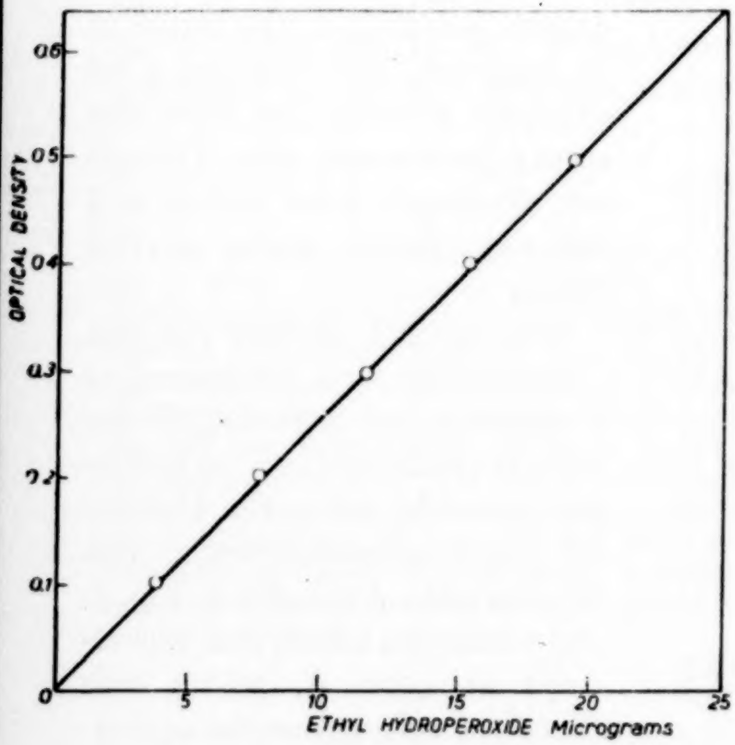

Fig. 3

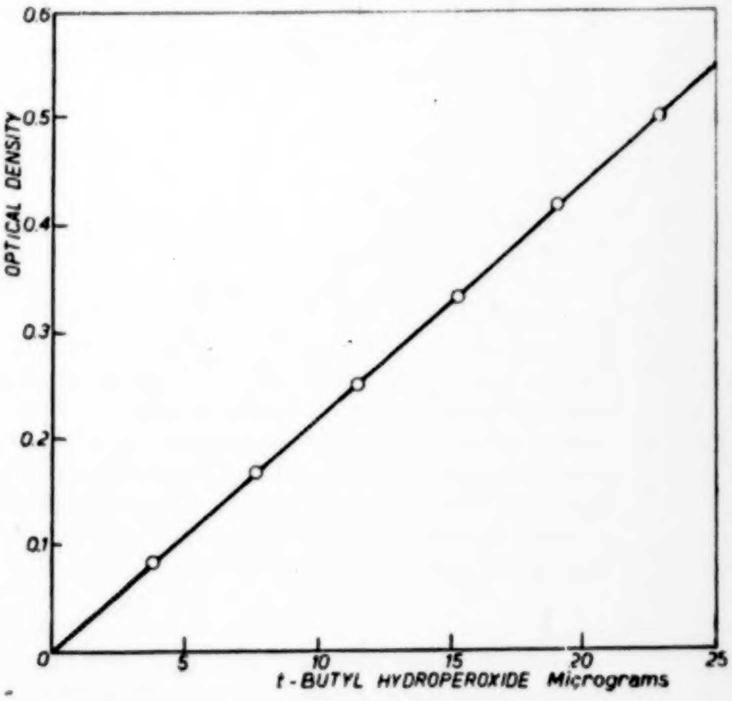

Fig. 4

References p. 428.

TABLE II

Molarity of Di-Ethyl Peroxide × 10^4 A	B	A/B	Found
22.0	11.0	2.0	2.2
1.11	0.55	2.0	2.0
2.22	0.55	4.0	4.2

Titanous sulphate method. The titanous sulphate method has been re-examined in some detail, since it is both simple and rapid to use, and is unaffected by atmospheric oxygen. The effect of varying the concentrations of the constitutents has been fully investigated and the optimum concentrations deduced. As a result of these experiments, the reagent is now made up by adding 20 ml of concentrated sulphuric acid to 2 ml of 10% titanous sulphate and making up to 100 ml with water. Dilute hydrogen peroxide is then added drop by drop until the bluish colour has changed to a faint yellow.

Since very weak solutions of hydrogen peroxide were to be analyzed, it was essential not to dilute them any more than was necessary. It was found that 1 ml of the reagent was sufficient to bring out fully the colour of 3 ml samples containing the hydrogen peroxide in the range to be analyzed. The resulting 4 ml of yellow solution just filled the spectrophotometer cells. The colour developed immediately and did not change during several hours.

The optical density of the yellow colour was determined as a function of wavelength for several concentrations of hydrogen peroxide, using the Unicam SP 500 spectrophotometer with 10 mm cells. As shown in Fig. 5, the maximum absorption was always at 4100 A, which was therefore selected as the operating wavelength.

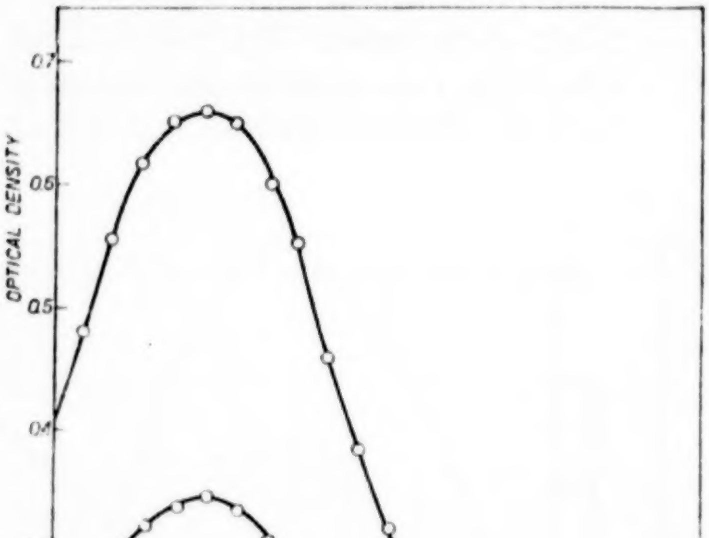

Fig. 5

References p. 428.

Beer's Law is accurately obeyed for optical densities up to 0.8, corresponding to a range of *ca.* 0.3 to 200 micrograms. (Fig. 6)

The colour developed from more concentrated solutions may be brought within this range by diluting the coloured solution. The lowest concentration which can be estimated is about 0.3 micrograms per ml, as compared with reported values of 2 micrograms per ml by EISENBERG[5], and 0.2 micrograms per ml in a cell four times longer by ALLSOPP[6], who, however, reported that Beer's Law was not accurately followed. When identical samples were estimated, the standard deviation was ±0.002, wich is equivalent to an error of 0.4%.

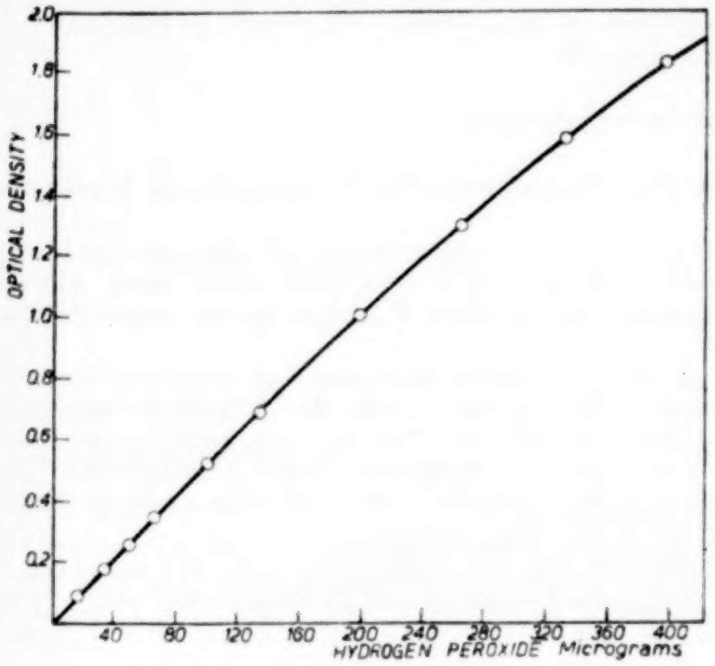

Fig. 6

Experiments with a reagent identical with the titanous sulphate one, but using instead the same concentrations of titanous chloride and of concentrated hydrochloric acid, showed that there was no significant difference in their analytical behaviour. Reagents used by some earlier workers, *e.g.* EGERTON, SMITH AND UBBELOHDE (*loc. cit.*), which were more dilute, were found not to develop fully the colour of very dilute samples.

SUMMARY

The conditions for the estimation of peroxides by three established methods have been re-examined in detail. 1. It is shown that the reduction of organic hydroperoxides by stannous chloride (BARNARD AND HARGRAVE method) can be carried out quantitatively and rapidly in alkaline solution. The advantages of this modification are discussed. 2. The exact conditions are described for accurately measuring the concentrations of hydrogen peroxide and of the lower organic peroxides by the thiocyanate method. Amyl alcohol is recommended as a decolourizer for the reagent since the red colour produced by the action of the peroxides is stabilized, permitting accurate spectrophotometric measurements. Using this reagent, 0.03 micrograms of peroxide per ml can be estimated. 3. The limits of the titanous sulphate method of estimating hydrogen peroxide have been determined and a method suitable for the determination of 0.3 micrograms of hydrogen peroxide per ml is described.

RÉSUMÉ

Les auteurs ont effectué une étude critique de 3 méthodes de dosage des peroxydes. 1. La réduction des hydroperoxydes organiques par le chlorure d'étain(II) (méthode de BARNARD ET HARGRAVE) peut être effectuée quantitativement et rapidement

References p. 428.

en solution alcaline. Les avantages de cette modification sont discutés. 2. Les conditions exactes sont décrites pour un dosage précis de peroxyde d'hydrogène et de peroxydes organiques inférieurs par la méthode au thiocyanate ferreux. On recommande d'éliminer la coloration rouge du réactif par extraction à l'alcool amylique; la coloration rouge produite par les peroxydes est stable, cette réaction permet des mesures spectrophotométriques précises. Il est possible de doser ainsi 0.03 µg de peroxyde par ml. 3. La méthode de dosage du peroxyde d'hydrogène au moyen de sulfate titaneux est examinée, et un procédé est décrit permettant de doser 0.3 µg de peroxyde d'hydrogène par ml.

ZUSAMMENFASSUNG

Die Bedingungen der Bestimmung von Peroxyden mit drei eingeführten Methoden wurden eingehend untersucht.

1. Es wurde gezeigt, dass die Reduktion der organischen Hydroperoxyde mit Stannochlorid (Methode von BARNARD UND HARGRAVE) quantitativ und schnell in alkalischer Lösung durchgeführt werden kann. Die Vorteile dieser Abänderung werden besprochen.
2. Die genauen Bedingungen zur genauen Konzentrationsmessung von Wasserstoffsuperoxyd und den niedrigen organischen Peroxyden nach der Rhodanidmethode werden beschrieben. Amylalkohol wird als Entfärber für das Reagenz empfohlen, da es die durch die Einwirkung der Peroxyde erzeugte rote Farbe stabilisiert und so genaue spektrophotometrische Messungen erlaubt. Bei der Benützung dieses Reagenzes können 0.03 µg Peroxyd/ml bestimmt werden.
3. Die Grenzen der Titan-II-sulfatmethode zur Bestimmung von Wasserstoffsuperoxyd wurden bestimmt und eine geeignete Methode zur Bestimmung von 0.3 µg Wasserstoffsuperoxyd/ml wurde beschrieben.

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ANALYSIS OF BERYLLIUM CARBIDE

by

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The determination of the composition of beryllium carbide was a major problem during studies directed toward the development of an improved method for its synthesis. Beryllium carbide is usually prepared by heating an intimate mixture of beryllia and lampblack in a protecting atmosphere of hydrogen or argon. The final product contains, in addition to some unreacted beryllia and carbon, traces of moisture and nitrides due to impurities in the protecting atmosphere. An analytical scheme to determine the total composition of experimental batches of this material, therefore, requires the following groups of determinations: (1) combined (*carbide*) carbon, to fix the quantity of beryllium carbide formed; (2) free carbon, beryllium oxide, nitrogen, and moisture, to indicate the total of impurities in the sample; and (3) total beryllium, to give a material balance.

Beryllium oxide and free carbon are the major impurities. Free carbon can be determined readily by conventional techniques, but a quantitative estimation of the beryllium oxide is difficult because the carbide and the oxide are attacked by the same reagents. Acids or bases, for example, which quantitatively decompose beryllium carbide also attack the beryllia to some extent[1]; and the temperature at which the beryllia is fired, either prior to or during the carbide synthesis, affects its solubility in most reagents[2]. Because of these factors, the use of the previously reported methods employing gaseous chlorine[7] or halogen acids[5,9] for the determination of oxides in similar materials is impractical.

A small amount of beryllium oxide as an impurity of beryllium carbide can be quantitatively measured by brominating the carbide. The technique is similar to that described by LILLENDAHL[7] for determining zirconium oxide in zirconium

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** Present Address: 125 Pecan Avenue, Magnolia, Arkansas metal by the use of purified chlorine gas. In the absence of moisture the reaction may be represented as:

$$(Be_2C + BeO) + 2Br_2 \rightarrow BeO + 2BeBr_2 + C$$

Beryllium bromide, which is volatile at the reaction temperature, can be swept from the bromination apparatus with dry argon, leaving carbon and the unreacted BeO. Ignition of the carbon leaves only BeO, which can be readily weighed.

Conventional combustion techniques are not suitable for the direct determination of combined (*carbide*) carbon in beryllium carbide. The prohibiting factor is the presence of two forms of free carbon in the material. One phase, an homogeneous mixture of beryllium carbide and amorphous carbon, arises from an incomplete reaction of beryllia and lampblack during synthesis. The quantitative estimation of amorphous carbon by combustion in oxygen is unreliable because the carbide is also partially decomposed at the temperatures necessary to effect complete combustion of the amorphous carbon. A graphitic form of carbon, a separate phase, remains stable in oxygen at temperatures up to those required to decompose the carbide itself.

The carbide carbon can be approximated indirectly by subtracting the free carbon content of the sample from the total carbon determined through combustion in an induction furnace. However, induction heaters are costly and a direct determination is always desirable. The method proposed here, whereby the carbide carbon is hydrolyzed to methane before combustion, is based on the fact that beryllium carbide, like aluminum carbide, liberates only methane on hydrolysis[8]. With the proper choice of catalyst, this methane can be quantitatively oxidized to carbon dioxide which then can be absorbed in Ascarite and weighed. The free carbon, which is not attacked during hydrolysis, may be filtered off and then ignited to carbon dioxide.

Beryllium carbide takes up atmospheric moisture quite readily. Vapor pressure studies have shown this moisture to be present both in the absorbed and the combined states, the latter being a hydrate of beryllium oxide. On drying the material, the water of hydration is partially evolved before the absorbed water is completely removed. It is therefore not feasible to distinguish between the two forms by conventional analytical techniques. However, total moisture can be determined if the samples are dried above 650° C.

On hydrolysis, impure beryllium carbide gives off nitrogen only in the form of ammonia. X-ray patterns of the material show evidence of Be_3N_2 and at least one higher nitride, but no cyanide or amide forms have been found. The Kjeldahl method is therefore suitable for the nitrogen determination.

The procedure outlined for the total beryllium analysis is a modification of the pyrophosphate method described by CUPR[3]. By more precise control of pH and of ammonium ion concentration during the precipitation of beryllium ammonium phosphate, a considerable improvement in accuracy over that reported by CUPR may be obtained.

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SPECIAL APPARATUS AND MATERIALS

Beryllium oxide. The apparatus consisting of a gas purification train and a bromination unit is illustrated in Fig. 1.

To remove traces of oxygen and moisture, the argon is passed over copper wool (A), maintained at 450° C, and then through a tower of anhydrous magnesium perchlorate (B). The bromine reservoir (C) is fabricated from a 250 ml glass stoppered Pyrex flask. A 2 mm straight-bore stopcock is sealed in the tube that extends from the drying tower into the bottom of the bromine flask. In this manner the argon is used as the vehicle for carrying bromine vapor to the reaction tube. To sweep the system prior to use, or while drying samples before bromination, the argon by-passes the bromine reservoir and flows directly into the reaction tube by means of a 2 mm three-way stopcock sealed in the neck of the flask as shown.

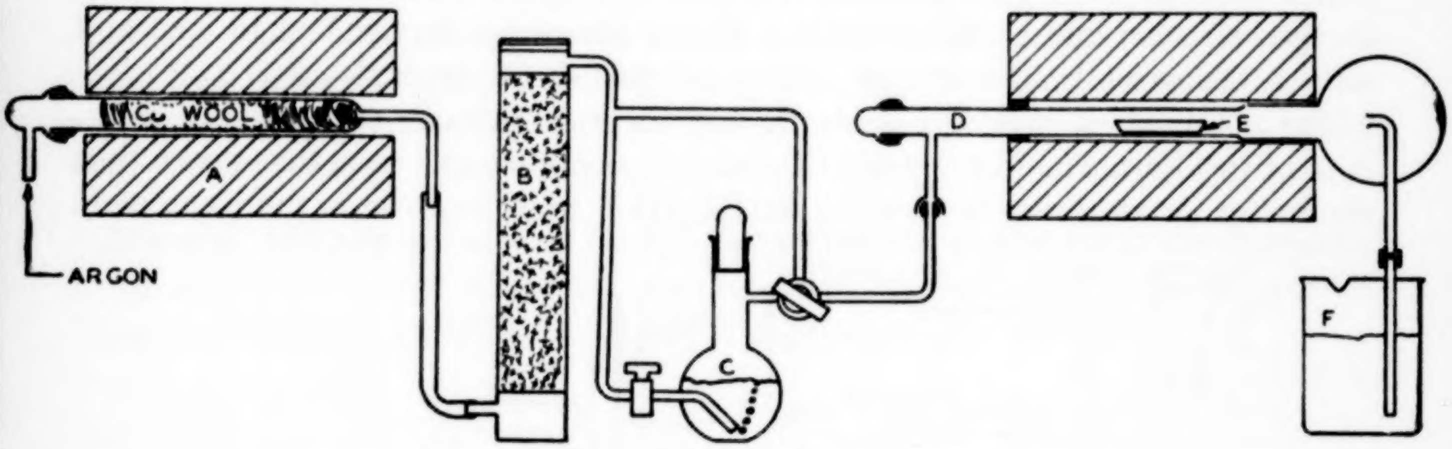

Fig. 1

The bromination tube (D) is made by sealing a 28/15 male ball joint to a quartz-borosilicate glass graded seal which is sealed in turn to a 19 mm i.d. Vycor tube extending from a 500 ml round bottom Vycor flask. A 9 mm tube sealed at the side of the Vycor flask extends into a beaker (F) containing a 50 per cent. solution of sodium hydroxide to neutralize any beryllium bromide or bromine which passes through the trap. The bromination tube is closed by a cap, blown from a 28/15 female ball joint, held securely in place by a spring clamp. The bromination tube is heated by a nichrome-wound resistance furnace which is controlled by a Variac. Samples are contained in a small silica boat (E) which is lined with a 1/4-inch bed of purified 40-mesh silica.

Traces of moisture and hydrobromic acid are removed from the bromine by adding 5 grams of anhydrous aluminum tribromide per pound to the liquid bromine in the reservoir.

The silica used for lining the boats must be purified by leaching in hydrochloric acid, followed by washing, drying and successive brominations at 900° C until constant weight is obtained. This treatment insures the absence of any organic material, moisture, or metals which form bromides.

The entire apparatus should be placed in a good hood since both beryllium bromide and bromine are toxic.

Combined carbon. A schematic diagram of this apparatus is shown in Fig. 2. The reaction flask is connected by a 28/15 ball joint to a reflux condenser. The condenser is so constructed that it permits the addition of acid and oxygen to the reaction flask and at the same time provides a closed system whereby the methane and oxygen may flow to the burner unit. The entrance to the combustion unit is packed with Pyrex wool, to trap any acid spray which may be carried by the gas stream; and is followed by a Pyrex frit sealed in the line to cool and diffuse the gases to prevent an accidental flash-back or explosion.

The combustion unit is essentially two identical burners connected in series. (Use of two burners and reversal of the direction of flow creates a turbulence that eliminates the tendency toward gas stratification, and thus insures more complete

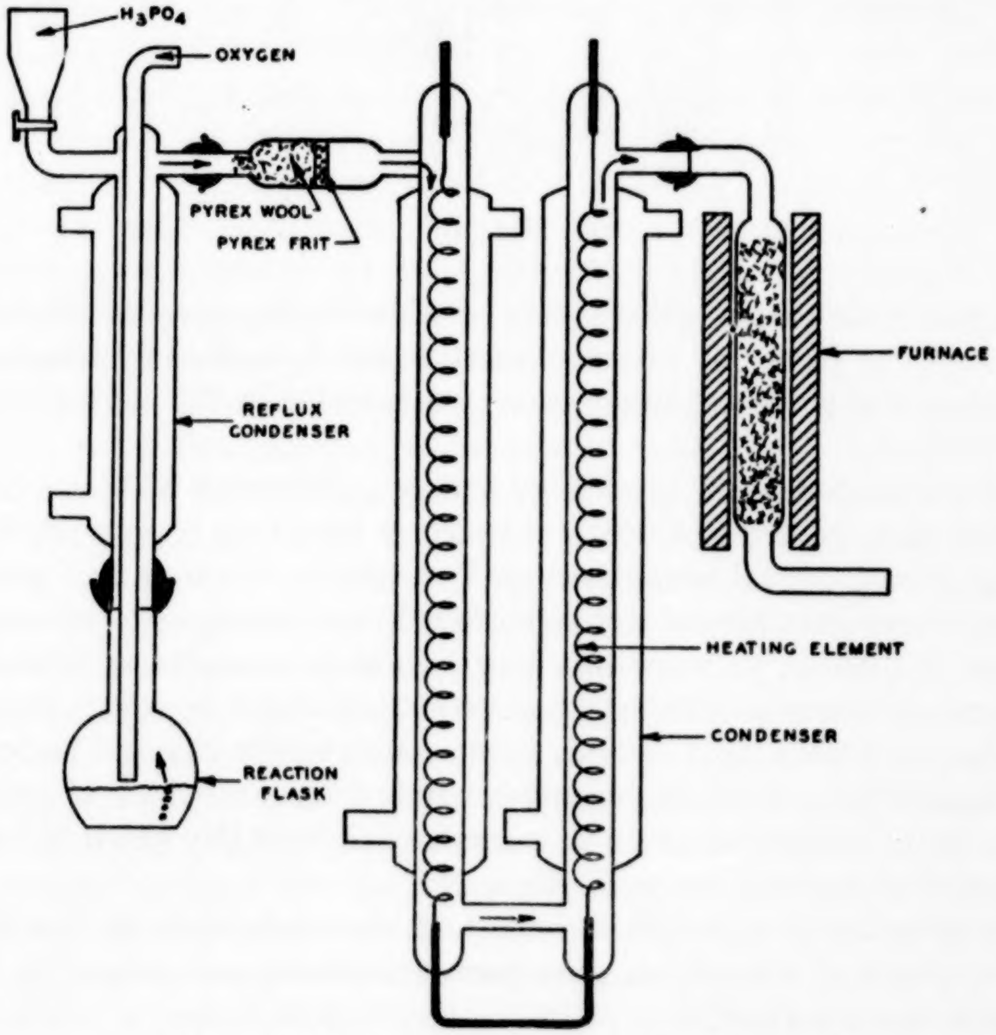

Fig. 2. Reaction flask and combustion unit.

combustion than that obtained by the use of a larger single unit). Each half of the methane burner is a water-cooled Pyrex condenser with a heating element running through the center from seals at each end. The heating element may be a 22 B & S gauge nichrome helix, silver soldered to 0.05 inch diameter platinum leads to seal through the glass, or it may be a helix of cobalt-plated 0.03 inch diameter platinum or platinum-rhodium wire with 0.05 inch diameter platinum leads. The operating temperature of this unit is 950°-1000° C.

A small furnace containing a tube of CuO, maintained at 350°-450° C, follows the combustion units to insure the oxidation of any carbon monoxide to carbon dioxide.

A U-tube containing anhydrous magnesium perchlorate, adjacent to the CuO burner exit, serves to dry the gases before they pass into a second tube containing Ascarite, where the carbon dioxide is collected for weighing. During operation, a small flow meter is attached to the exit of the Ascarite tube. The reaction flask may be heated by a small electric hot plate or a gas burner. The system is swept with CO_2-free oxygen at all times.

Nitrogen. The apparatus used for this determination is essentially the improved Kemmerer-Hallett type which has been modified by placing a 35/25 ball joint on the digestion flask to afford convenient loading of dry samples.

PROCEDURE

Sample preparation and storage. In hardness, beryllium carbide is comparable to diamond and severely scratches boron carbide or sapphire mortars. The use of a Plattner's diamond mortar for reduction of the particle size to pass a 200 mesh screen has proved most satisfactory. Samples prepared in this manner are stored in a well-desiccated atmosphere to prevent decomposition due to hydrolysis by atmospheric moisture.

Free carbon. Weigh a 150 mg sample of the carbide into a 1 ml beaker. Transfer the beaker with sample to a 125 ml iodine flask and add 50 ml of 1 : 1 sulfuric acid. Fit the flask with a water-cooled condenser and reflux the mixture on a hot plate until the sample dissolves. Filter the carbon and any insolubles into a fritted porcelain crucible of medium porosity. Wash thoroughly with a 1% sulfuric acid solution, and dry the residue by pulling air through the crucible for five minutes. Reserve the filtrate for beryllium analysis. Place the crucible and contents in a suitable combustion train. Ignite for one hour in a stream of oxygen at a temperature of 900° C and collect the evolved carbon dioxide in Ascarite. Free carbon is calculated from the weight of carbon dioxide collected:

$$\frac{\text{Wt. of } CO_2 \text{ (g)} \times 27.29}{\text{Wt. of Sample (g)}} = \text{Per cent. free carbon}$$

Total beryllium. The filtrate from the free carbon determination is transferred to a 250 ml volumetric flask and made up to volume with distilled water. A 100 ml aliquot of this solution is pipeted into a 400 ml beaker and three or four drops of methyl red indicator is added. Concentrated ammonium hydroxide is added to the acid solution until the indicator changes color and beryllium hydroxide begins to precipitate. The excess ammonium hydroxide is neutralized with dilute (1 : 20) sulfuric acid and the solution made slightly acid to the indicator. The solution is then made just basic to methyl red with dilute (1 : 20) ammonium hydroxide and 10 ml of 10% dibasic ammonium phosphate solution is added dropwise with stirring. The solution is again made just acid to the indicator by the addition of dilute sulfuric acid. At this point the total volume of the solution should be about 135 ml. The precipitate at this stage will be amorphous.

The slightly acid solution is now placed in a water bath and allowed to digest at a temperature of 95°-98° C for three hours. During this acid digestion period, the beryllium ammonium phosphate will change from an amorphous to a crystalline precipitate. At the end of the digestion period, the solution is diluted with hot water to approximately 230 ml and again made basic with dilute ammonium hydroxide; 3 ml excess of ammonium hydroxide is added. The basic solution is again digested in the water bath for two and one half hours. The solution is then removed and allowed to stand overnight.

The crystalline precipitate is collected on a Number 42 Whatman paper and washed with a hot one per cent. ammonium nitrate solution made basic to methyl red with dilute ammonium hydroxide. Washing is continued until a sample of the washings gives a negative test for the sulfate ion with a 5 per cent. solution of barium chloride.

The paper and precipitate are transferred to a pre-ignited and tared porcelain crucible. After the paper has been charred slowly, the precipitate is ignited for one hour at 1000° C in a muffle furnace. The crucible is cooled in a desiccator and weighed. The residue should be pure white in color. The per cent. beryllium is calculated as follows:

$$\frac{\text{Wt. of } Be_2P_2O_7(g) \times 2.5 \times 0.09396 \times 100}{\text{Wt. of Sample (g)}} = \text{Per cent. Be}$$

Beryllium oxide. Line a 4-inch silica boat to a depth of 1/4 inch with purified silica. Spread evenly over the surface of the silica bed not more than 200 mg of beryllium carbide. Place the boat in the cold bromination tube, adjust the argon flow rate to approximately 150 cc/min and heat the sample quickly (50°/min) to 825° C. Dry the sample at this temperature for ten minutes.

Rotate the three-way stopcock and open the straight-bore stopcock so that argon bubbles through the bromine. Brominate the sample for thirty minutes.

Adjust the stopcocks to allow the argon to by-pass the bromine flask. With argon still flowing, gradually raise the temperature to 950° C, and sweep the tube for an additional thirty minutes. Cool the system to 300° C, transfer the boat and its contents to a muffle furnace and burn off the carbon. Remove the boat, cool in a desiccator and weigh. The beryllium oxide contained in the sample is calculated by the equation:

$$\frac{\text{Wt. of BeO (g)} \times 100}{\text{Wt. of Sample (g)}} = \text{Per cent. BeO}$$

Combined carbon. A newly assembled apparatus should be swept with oxygen for at least an hour with the burner and copper oxide furnace at operating temperatures. After the burner is conditioned, the system is swept for one hour with oxygen and a blank is determined.

A 50-100 mg sample of the carbide is weighed into a 1 ml beaker and placed in the dry reaction flask. A tared Ascarite tube is placed in the train and 25 ml of 85 per cent. orthophosphoric acid is added through the small funnel. After the stopcock on the funnel is closed, the oxygen flow-rate is adjusted to 30-50 cc/min for a nichrome burner or 125-150 cc/min for a cobalt-platinum burner.

The flask is heated slowly. When the reaction begins, the heater is withdrawn until the methane evolution nearly ceases. This action is repeated until the reaction is complete. Finally, the solution is boiled and the system is swept for an additional twenty minutes. The Ascarite tube is then weighed.

$$\text{Calculation: } \frac{\text{Wt. of } CO_2 \text{ (g)} \times 27.29}{\text{Wt. of Sample (g)}} = \text{Per cent. Combined Carbon}$$

If the apparatus is functioning properly, blanks are negligible and need not be considered in making the calculation. High blanks usually result from carbon dioxide dissolved in the phosphoric acid. This source of error can be eliminated by boiling the acid prior to use.

Nitrogen. Place a 100 mg sample of the carbide in the dry digestion flask, and fit the flask securely to the system with a spring clamp. The condenser tip should dip just below the surface of 25 ml of standard 0.01*N* sulfuric acid in the receiver flask. Add 30 ml of a 50 per cent. solution of sodium hydroxide to the digestion flask. Close the pinch clamp on the steam generator and allow steam to bubble into the digestion flask. Continue the steam distillation until approximately 100 ml of distillate has been collected, but maintain the volume of liquid in the digestion flask at a minimum throughout the distillation. Wash down the tip of the condenser with distilled water and boil the acid solution for one or two minutes. Cool the solution to room temperature and titrate with standard 0.01*N* sodium hydroxide to a faint yellow end-point of the methyl red. Nitrogen is calculated by the equation:

$$\text{Per cent. Nitrogen} = \frac{(\text{ml } H_2SO_4 \times N\ H_2SO_4) - (\text{ml NaOH} \times N \text{ NaOH}) \times 1.4}{\text{Wt. of Sample (g)}}$$

Moisture. Weigh out a 150 mg sample of carbide into a small porcelain or platinum boat, and place the boat in an appropriate drying train. Heat the sample for one hour at 700° C in a stream of dry argon and collect the evolved water in Anhydrone. The per cent. moisture is calculated as follows:

$$\frac{\text{Wt. gain of Anhydrone tube (g)} \times 100}{\text{Wt. of Sample (g)}} = \text{Per cent. Moisture}$$

EXPERIMENTAL

The experimental work leading to the development of the beryllium oxide method included a study of the effect of bromine at elevated temperatures on silica, graphite and platinum boats. Of the three materials tested, only silica proved to be satisfactory, since both platinum and graphite boats suffered a pronounced loss in weight during repeated brominations.

A series of bromination tests was also made on samples of "fluorescent grade" beryllium oxide to ascertain its stability in an atmosphere of bromine at 750°-1050° C. The oxide is very stable in bromine up to 850° C, but it is slightly attacked at 900° C. All later brominations were, therefore, made between 825°-850° C.

Excellent recoveries were obtained when synthetic samples of beryllium carbide, containing 19.00 per cent. "fluorescent grade" BeO (Bureau of Standards Sample No. 2686), were subjected to thirty-minute brominations at 850° C. The results of these tests are given in Table I.

TABLE I

BeO RECOVERIES ON SAMPLES OF Be_2C AFTER A THIRTY-MINUTE BROMINATION

Weight of sample (gram)	Weight of oxide recovered (gram)	BeO (per cent.)
0.1453	0.0275	18.93
0.1421	0.0268	18.86
0.1491	0.0283	18.98
0.1443	0.0274	19.01

Because nominal beryllium carbide contains varying amounts of moisture and beryllium nitrides, tests were made to ascertain that the bromination method gave quantitative results with these impurities present. Wet samples, placed in a bromination unit, previously heated to 850° C, gave consistently high results due to hydrolysis of the beryllium bromide formed during the reaction. This source of error was readily eliminated by drying the samples in the bromination apparatus itself. The samples were placed in the cold tube, which was then slowly raised to 850° C before proceeding with the bromination.

Beryllium nitride alone was found to react very readily with bromine in the desired temperature range and to decompose to volatile products which were easily swept from the reaction tube. In a series of tests, samples of carbide mixed with varying percentages of beryllium nitride and known amounts of beryllium oxide brominated easily; and a quantitative recovery of oxide was obtained in every case.

Additional tests using the outlined procedure were made to study the reproducibility of the method. Results of these tests are given in Table II.

TABLE II

REPRODUCIBILITY OF THE BROMINATION METHOD

Sample No.	Wt. of Be_2C (gram)	BeO recovered (per cent.)	Deviation from mean
1 a	0.0913	1.01	—0.01
1 b	0.1034	0.97	—0.05
1 c	0.1854	1.02	0.00
1 d	0.0954	1.06	0.04
2 a	0.1443	3.88	0.13
2 b	0.0993	3.73	—0.02
2 c	0.7140	3.75	0.00
2 d	0.1152	3.64	—0.11
3 a	0.0978	2.66	—0.06
3 b	0.1119	2.86	0.14
3 c	0.1859	2.64	—0.08
4 a	0.1352	9.39	0.06
4 b	0.1554	9.40	0.07
4 c	0.2175	9.33	0.00
4 d	0.2018	9.22	—0.11
4 e	0.1630	9.33	0.00

Development of the procedure for combined carbon included tests to establish the absence of any other gaseous hydrocarbons in the methane from acid hydrolysis of beryllium carbide. A spectrographic examination of the beryllium carbide indicated that metallic contaminants capable of forming carbides either were absent or were of such a small magnitude that they contributed only a negligible error. Samples of several batches of the carbide were heated in a closed system with phosphoric acid and the gas evolved was collected over water in a gas burette.

The burette was then connected to an Orsat apparatus and the gas was analyzed in the usual manner. No unsaturated hydrocarbons were found, and data obtained from combustion of the purified gas indicated that only methane was present. Other samples of carbide were decomposed by acid hydrolysis and their combined carbon contents were calculated from the weights of carbon dioxide collected in the proposed apparatus. Samples from the batches of carbides were also analyzed using the Orsat method. A comparison of these data is shown in Table III.

TABLE III

COMPARISON OF CATALYTIC COMBUSTION VS. GASOMETRIC METHOD FOR COMBINED CARBON

Trial	Be_2C Taken (g)	cc of CH_4 collected (S.T.P.)	Combined carbon equivalent (per cent.)	Combined carbon by combustion analysis (per cent.)
1 a	0.0504	34.13	36.3	36.4
1 b	0.0548	37.14	36.4	
2 a	0.1307	78.81	32.3	32.7
2 b	0.0915	55.36	32.5	
3 a	0.0492	33.75	36.8	36.9
3 b	0.0423	29.32	37.2	
4 a	0.0693	41.54	32.1	32.5
4 b	0.0693	41.60	32.1	

It should be noted that in making these comparisons the accepted error in reading a gas burette will change the calculated carbon content shown above by as much as ± 0.1 per cent.

Initial investigation of the feasibility of quantitatively burning methane was preceded by a literature search on effective catalysts for this oxidation. YANT AND HAWK[10], FISCHER AND TROPSCH[4], KLYUKVIN AND KLYUKVINA[6], and YOSHIKAWA[11] have investigated the catalytic efficiency of various materials for the oxidation of methane. In every case, cobalt was judged best with nickel a close second. Iron oxide was also found to have some catalytic activity by those who included it in their studies. Investigations in this laboratory confirmed these conclusions. Ordinary nichrome heating elements in the combustion unit were found to be effective catalysts, and cobalt plated on platinum was found to be much more efficient than nickel plated on platinum. A comparison of combined carbon values obtained by using four types of heating elements for analyzing the same sample is given in Table IV.

TABLE IV

COMPARISON OF BURNER ELEMENTS FOR COMBINED CARBON DETERMINATION

Nichrome	Cobalt-plated platinum	Nickel-plated platinum	Platinum
38.04	38.03	36.79	25.74
38.33	37.86	35.33	35.58
38.04	37.95	35.66	42.02
38.22	37.84	43.67	35.80

Nickel-plated platinum and bare platinum give erratic results. These were caused by incomplete methane oxidation resulting in a deposit of carbon on the cooled walls of the combustion unit during some determinations and by subsequent dislodging and combustion of the carbon in later determinations.

The data given in Table IV show that either nichrome wire or cobalt-coated platinum wire can be used. The factors which must be considered in making a choice are evident. The cost of the nichrome helix is negligible but durability of the burner is desirable. For a reasonable length of service, the nichrome elements should not be operated above 900° C, but to obtain complete methane combustion at this temperature the oxygen flow-rate must be exceedingly slow (30-50 cc/min). Operating at a low flow-rate necessitates very careful control during decomposition, because the methane must be generated so slowly that the oxygen-methane mixture never contains more than four per cent. methane. Oxygen and methane form an explosive mixture when the methane concentration is between four and fifteen per cent.

The cost of the platinum and the additional effort required to plate it with cobalt are the chief deterrents to its use, but with a platinum burner an element temperature of approximately 1100° C is possible and the gas flow may safely be set at 150 cc/min. With the increased flow-rate of oxygen, the decomposition rate of the sample can also be increased and thus effect a saving of time for the analysis.

Nichrome units heated to 850°-900° C will operate continuously for more than six months without failure. The average time required per analysis is one and one half hours. Cobalt-plated platinum spirals, however, have been operated continuously at 1000°-1100° C for over a year and their use has reduced the average analysis time to approximately forty-five minutes. The extreme temperature gradients in the walls of these combustion units do not impair their longevity.

It is by far more common to add a new heating spiral to the old apparatus than to rebuild the entire glass system. Proper choice of acid for dissolving samples is a further aid in prolonging the life of these burners. Orthophosphoric acid is preferable to either sulfuric or hydrochloric acids because traces of gaseous hydrogen chloride severely poison the hot catalysts and sulfuric acid forms an explosive mixture with the methane.

To further establish the validity of this analytical scheme, the analysis for total carbon was compared with the sum of the analyses for carbide carbon and free carbon. The carbide carbon was determined by the above method. Free carbon was determined by digesting separate portions of carbide in 1 : 1 sulfuric acid, collecting the insoluble carbon in a fritted crucible and burning it to carbon dioxide. Determinations of total carbon were made with an induction furnace, using oxygen and an iron-tin flux. These data are given in Table V.

TABLE V

COMPARISON OF TOTAL CARBON WITH FREE AND COMBINED CARBON

Sample No.	Free carbon (per cent.)	Combined carbon (per cent.)	Total carbon calc. (per cent.)	Total carbon found (per cent.)
1	4.21	31.57	35.78	35.78
	4.22	31.49	35.71	35.74
			Av. 35.75	35.76
2	0.92	36.48	37.40	37.27
	1.00	36.45	37.45	37.34
	1.03	36.40	37.43	37.45
			Av. 37.43	37.35
3	1.49	33.92	35.41	35.45
	1.45	33.94	35.39	35.31
			Av. 35.40	35.38

TABLE VI

COMPOSITION OF TYPICAL PRODUCTION SAMPLES

Batch No.	Combined carbon (per cent.)	Free carbon (per cent.)	BeO (per cent.)	Nitrogen (per cent.)	Total beryllium (per cent.)	Moisture (per cent.)	Total analysi (per cen
824	37.90	0.96	1.21	1.50	58.81	0.10	100.04
544	35.49	1.22	5.31	2.25	57.21	0.76	100.33
1237	37.67	2.04	0.20	1.64	58.59	0.25	100.32
1300	36.29	0.57	1.72	2.72	58.57	1.10	100.35
1290	37.29	0.87	2.57	1.16	57.74	1.39	100.09
19-0	34.78	1.22	8.53	1.40	56.94	0.61	99.87
G-36	35.87	1.28	4.36	1.36	58.82	0.02	100.32
J-73	34.78	3.13	2.27	0.22	59.66	1.00	100.24
120-B	29.19	9.91	10.36	4.10	49.55	0.51	99.89
1854	16.11	9.74	29.23	2.30	33.16	19.97	99.97

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DISCUSSION

No standard samples of beryllium carbide are available; and since the pure compound has never been made, the preparation of synthetic samples was not possible. During experimental tests, known amounts of beryllium oxide, nitride and carbon were blended with the highest purity carbide obtainable. Twelve control samples, prepared in this manner, have also been analyzed concurrently with regular production samples for over a year. During this period an accurate record of the results has shown the reproducibility of the determinations to be excellent. The results of the analysis of ten production samples chosen at random are tabulated in Table VI. Each determination shown was run in duplicate. The average total analysis time per sample was nineteen hours.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the assistance of Dr. MILTON GALLAGHER and L. M. STECKEL of the Industrial Research Institute, Chattanooga, Tennessee, in modifying the procedure for the total beryllium analysis.

SUMMARY

An analysis scheme is presented for determining the composition of impure beryllium carbide. The determination of combined (*carbide*) carbon, which fixes the amount of Be_2C present, is based on a catalytic oxidation of the methane formed by an acid hydrolysis of the carbide. The major impurities, beryllium oxide and free carbon, are readily determinable after separating the oxide by selective bromination of the carbide, and liberating the free carbon by a simple acid digestion. Analysis for fixed nitrogen is made by the Kjeldahl method and total moisture, which includes both adsorbed water and water of hydration, is obtained by drying samples in an inert gas stream at 700° C. An improved dibasic ammonium phosphate precipitation is used for determining beryllium.

RÉSUMÉ

Un schéma d'analyse est proposé pour déterminer la composition du carbure de béryllium impur. Le dosage du carbone combiné (carbure) donnant la teneur en Be_2C présent est basé sur l'oxydation catalytique du méthane formé par hydrolyse acide du carbure. Les principales impuretés, oxyde de béryllium et carbone libre, sont dosées après séparation de l'oxyde par bromuration sélective du carbure et libération du carbone libre par une simple digestion acide. L'analyse de l'azote fixé est faite par la méthode de Kjeldahl, et l'humidité totale comprenant l'eau adsorbée et l'eau d'hydratation, est déterminée par séchage de la substance dans un courant de gaz inerte à 700° C. Le béryllium est dosé par précipitation au phosphate diammonique.

ZUSAMMENFASSUNG

Ein Analysenschema zur Bestimmung der Zusammensetzung von unreinem Berylliumcarbid wird vorgelegt. Die Bestimmung von gebundenen (Carbid-) Kohlenstoff, die die anwesende Menge Berylliumcarbid ergibt, ist auf die katalytische Oxydation des bei der Saürehydrolyse des Carbids gebildeten Methans gegründet. Die Hauptverunreinigungen, Berylliumoxyd und freier Kohlenstoff, sind nach der Abtrennung des Oxyds durch selektive Bromierung des Carbids und Freisetzung

des freien Kohlenstoffs durch eine einfache Säuredigestion leicht zu bestimmen. Die Kjeldahlmethode ergibt den fixen Stickstoff. Das Gesamtwasser (sowohl absorbiertes, wie Kristallwasser) erhält man durch das Trocken der Proben in einem inerten Gasstrom bei 700°. Eine verbesserte Ausfällung mit zweibasischem Ammoniumphosphat wird zur Bestimmung von Beryllium benützt.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES
LXIII. DOSAGE DU PLATINE*

par

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On a proposé de doser gravimétriquement le platine après précipitation avec les substances suivantes:

Magnésium
Hydrogène sulfuré
Sel d'ammonium
Sel de potassium
Sel de rubidium
Sel de césium
Sel de thallium

Thioformamide
Thiophénol
Thiosemicarbazide
Bromure de tétraphénylarsonium
α-Furiledioxime

Les courbes de thermolyse des précipités correspondants ont été préparées avec la thermobalance à enregistrement photographique sur des poids moyens de 200 mg. Tous les chauffages ont été faits dans l'air et non dans l'hydrogène, suivant une loi linéaire et à la vitesse de 300° par heure.

Si nous n'avons pu reproduire les affirmations des auteurs en ce qui concerne les méthodes au platibromure de tétraphénylarsonium et à la furiledioxime, nous sommes, il est vrai, en mesure de proposer une nouvelle méthode gravimétrique utilisant le thiophénol, par analogie avec ce que nous avions déjà remarqué à propos du dosage de l'or.

A. Réduction en métal par le magnésium

Parmi les nombreuses méthodes préconisées pour faire la précipitation du platine à l'état métallique, nous avons suivi celle de SCHEIBLER[1]. La solution

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* Pour LXII (Yttrium), voir *Anal. Chim. Acta,* 10 (1954) 321.

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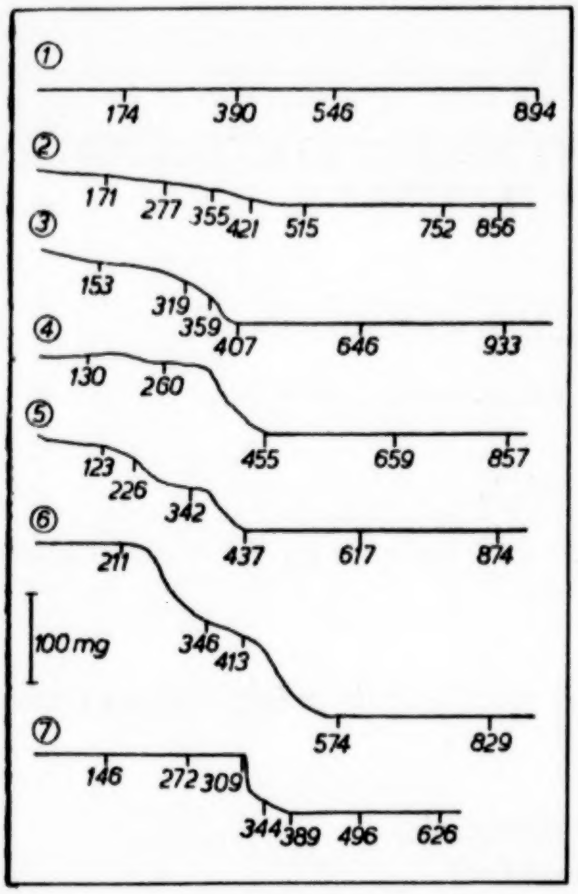

Courbes de thermolyse des dérivés du platine

Fig. 1. Platine précipité par le magnésium.
Fig. 2. Sulfure?
Fig. 3. Précipité avec le thioformamide.
Fig. 4. Thiophénolate.
Fig. 5. Précipité avec la thiosemicarbazide.
Fig. 6. Précipité avec le bromure de tétraphénylarsonium.
Fig. 7. Précipité avec l'α-furiledioxime.

neutre du sel de platine est traitée par un copeau de magnésium. On chauffe et dissout l'excès de ce métal dans l'acide acétique étendu. Nous avons l'impression que cette dissolution n'est pas totale et qu'une trace de magnésium reste mélangée au platine. La courbe représentative (Fig. 1) est sensiblement linéaire. On observe, à partir de 646°, un léger gain de poids qui s'élève à 1/200 au voisinage de 900°. Il y a tout intérêt à effectuer le séchage entre 100 et 600°.

B. Précipitation en sulfure

La solution chaude, non azotique, du sel de platine est traitée par un courant d'hydrogène sulfuré[2]; on filtre et réduit le précipité par la chaleur. La courbe de thermolyse (Fig. 2) est sans cesse décroissante jusqu'à 421° sans que l'on puisse apercevoir de palier horizontal relatif à un sulfure défini. Au-dessus de cette température et jusqu'à 954°, la courbe se maintient parfaitement horizontale. Le produit sec de départ ne correspond pas non plus à la formule PtS_2 mais renferme un excès de soufre. La méthode peut servir pour le dosage automatique mais au-dessus de 421° seulement.

C. Précipitation sous forme de platichlorures

Nous avons reproduit les précipitations sous forme de platichlorures divers qui se laissent peser à basse température sauf celui d'ammonium. On se reportera aux courbes de thermolyse déjà tracées[3].

D. Précipitation par le thioformamide

Nous avons suivi la méthode récente de GAGLIARDI ET PIETSCH[4] mais sans filtrer sur pulpe de papier. Le précipité obtenu est un mélange qui perd du poids dès la température ordinaire avec inflexion entre 100 et 153°. A partir de 407°, on obtient le platine à poids constant. Il est inutile de chauffer à 950° comme

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l'indique le mémoire. Comme dans le cas du platichlorure d'ammonium, le noir de platine libéré se montre très oxydable au-dessus de 625°.

E. Précipitation par le thiophénol

En se servant d'un réactif neuf, non oxydé et en opérant suivant la technique de CURRAH, MCBRYDE, CRUIKSHANK ET BEAMISH[5], nous avons obtenu un précipité vert-jaune qui se comporte exactement comme celui de l'or. La courbe de thermolyse (Fig. 4) montre qu'entre 230 et 300°, le précipité présente un poids bien constant qui s'accorde avec la formule $Pt(C_6H_5\text{-}S)_2$ (donc à base de platine bivalent) à moins de 1/1000 près. Ce dérivé de platine est donc beaucoup plus stable que celui d'or monovalent qui se décomposait, rappelons-le, entre 157 et 187°. Ici, la décomposition a lieu entre 300 et 455°. Le platine résiduel ne gagne pas de poids lorsqu'on le chauffe jusqu'à 960° (analogie avec l'or). Le précipité de thiophénolate platineux est recommandé pour le dosage automatique du platine. Le facteur analytique vaut 0.4698. Comme dans le cas de l'or, les homologues du thiophénol que nous avons essayés pour diminuer encore ce facteur, se montrent moins avantageux du point de vue stabilité et du point de vue précipitation que le thiophénol lui-même.

F. Précipitation avec la thiosemicarbazide

Nous avons opéré d'après NAITO, KINOSHITA ET HAYASHI[6]; le précipité bleu résultant ne paraît pas posséder une formule définie; il perd du poids dès la température ordinaire et, comme le montre la courbe de la Fig. 5, le platine est obtenu à poids constant à 437° seulement.

G. Précipitation avec le bromure de tétraphénylarsonium

Le précipité orangé réalisé sur des poids compris entre 5 et 20 mg de platine, d'après les indications de BODE[7] a conduit à des courbes analogues à celle de la Fig. 6. Ces courbes présentent, en général, un palier de poids constant s'étendant jusque vers 210° tandis que le platine résultant de la décomposition prend naissance entre 540° et 550° et n'est pas réoxydable. Malheureusement, nos essais ne s'accordent avec aucune formule définie pour le précipité desséché à 110°. Tantôt, son poids est supérieur à celui qui correspond à la formule attendue $[PtBr_6][(C_6H_5)_4As]_2$ et l'on peut croire qu'il retient du réactif par adsorption, tantôt, il est inférieur à celui qui correspond même à $PtBr[(C_6H_5)_4As]_2$. La méthode ne nous paraît donc pas correcte et ne présente aucun avantage sur les autres si l'on doit peser sous forme de platine. Il faudrait que l'auteur précise son mode opératoire puisque trois investigateurs différents trouvent des nombres très discordants quoique le platine soit chaque fois complètement précipité. Nous n'envisageons cette méthode, jusqu'à plus ample informé, qu'à titre de séparation.

H. Précipitation par l'α-furiledioxime

La méthode suivie est due à Ogburn[8]. Le précipité obtenu ne correspond pas à une formule définie et retient beaucoup moins d'une molécule-gramme de dioxime par atome-gramme de platine mais tout le métal est précipité. La courbe de thermolyse (Fig. 7) réalisée avec le précipité nous indique cependant un palier horizontal jusqu'à 309°; il se produit alors une destruction brusque et l'on arrive au platine métallique au-dessus de 370°. Nous conservons à la méthode son caractère de séparation.

TABLEAU RÉCAPITULATIF

Le tableau suivant contient un résumé des méthodes de dosage gravimétrique du platine avec les formes de pesée et les limites de température acceptables pour les dessiccations avec les poids utilisés. Les procédés proposés pour le dosage automatique sont indiqués par un astérisque.

Réactif précipitant	Forme de pesée	Limites de température
Magnésium	Pt	100 — 600°
*Hydrogène sulfuré	Pt	au-dessus de 421°
Sel d'ammonium	Pt	407 — 538°
*Sel de potassium	$[PtCl_6]K_2$	54 — 270°
*Sel de rubidium	$[PtCl_6]Rb_2$	70 — 674°
*Sel de césium	$[PtCl_6]Cs_2$	200 — 409°
*Sel de thallium	$[PtCl_6]Tl_2$	65 — 155°
Thioformamide	Pt	407 — 625°
*Thiophénol	$[C_6H_5S]_2Pt$	230 — 300°
Thiophénol	Pt	au-dessus de 455°
Thiosemicarbazide	Pt	au-dessus de 437°
Bromure de tétraphénylarsonium	Pt	au-dessus de 550°
α-Furiledioxime	Pt	au-dessus de 370°

REMERCIEMENTS

Nous voulons exprimer notre gratitude au Dr. Ng. Dat Xuong qui s'est chargé d'effectuer quelques synthèses particulièrement délicates de réactifs organiques et à Mlle Colette Wadier qui a réalisé les courbes de thermolyse.

RÉSUMÉ

Les auteurs ont étudié les courbes thermogravimétriques des précipités proposés pour doser le platine. Ce métal précipité est, comme l'or, tantôt oxydable, tantôt déposé à poids constant. Le thiophénolate de platine bivalent, isolé par les auteurs, se prête à une excellente gravimétrie; après quoi, vient la pesée des platichlorures.

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SUMMARY

The authors have studied the thermogravimetric curves of precipitates proposed for the determination of platinum. This precipitated metal is, like gold, sometimes oxidisable, sometimes deposited at constant weight. Bivalent platinum thiophenolate, isolated by the authors, is excellently suitable for gravimetry, after which comes the weighing as platinum(II) chlorides.

ZUSAMMENFASSUNG

Die Autoren untersuchten die thermogravimetrischen Kurven der zur Bestimmung von Platin vorgeschlagenen Ausfällmittel. Das ausgefällte Metall ist wie Gold manchmal oxydierbar, manchmal in konstanten Gewichtsmengen niedergeschlagen. Das von den Autoren isolierte Thiophenolat des zweiwertigen Platins eignet sich ausgezeichnet zur gravimetrischen Bestimmung, danach kommen Platinichloride.

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A SIMPLE CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF THE SATURATED STRAIGHT-CHAIN FATTY ACIDS C_{10}-C_{24}

by

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INTRODUCTION

During the last years several chromatographic methods have been described for the separation of the fatty acids through C_{10}, using silicagel as carrier and different solvents as immobile and mobile phases. In general, it can be stated that the most critical requirement of these chromatographic methods is a suitable silicagel. In 1951 we described[1] a semimicro method for the determination of the volatile fatty acids C_4-C_{10} and in the same publication a description is given of the preparation of a silicagel, which proved to be highly suitable for the separation of these acids. In that method, which is based on the principle of RAMSEY AND PATTERSON[2], the fatty acids through C_{10} are separated on a column of silicic acid, using methanol as the immobile solvent, *iso*octane as the mobile solvent and bromocresol green as the indicator. In our hands this method never failed to give excellent results, which was mainly due to the qualities of the gel.

Apparently it is a more difficult problem to work out a simple and accurate method for the separation of the higher acids (C_{10}-C_{20} and higher). RAMSEY AND PATTERSON[3] were able to separate the C_{11}-C_{19} acids virtually quantitatively on a silicagel column by using a mixture of furfuryl alcohol and 2-aminopyridine as the immobile solvent with *n*-hexane as the mobile phase. In this method, however, the position of the acids on the column can not be demonstrated with the aid of an indicator, firstly since the acids of this series are too weak to give a colour change with bromocresol green and secondly because of the presence of the basic 2-aminopyridine in the immobile phase. Therefore it is necessary in this method to titrate a large number of small percolate fractions, which is time-consuming and inevitably causes some inaccuracy. To obtain one accurate titration for each acid RAMSEY AND PATTERSON collect the titrated fractions of each acid and, after distilling to dryness, dissolving in water, acidifying, extracting with ether and evaporating, the residue is dissolved in ethanol and titrated. Though the publicated results proved to be very satisfactory, this method must be considered rather laborious.

BOLDINGH[4] introduced the reversed phase chromatography for the separation of the fatty acids. Undoubtedly this method, which covers a wide range of acids ($\pm C_8 — \pm C_{24}$), is very promising. A modification of the method (not yet published) is applied in several laboratories in the Netherlands with satisfactory results. In this method Hevea rubber is used as a support for a nonpolar solvent and a polar solvent is run through the column as the mobile phase. However, in this method too the acids on the column are invisible, so that a large number of titrations are necessary.

Since our method for the separation and determination of the C_4-C_{10} acids is quick, accurate and simple, we tried to work out an identical separation method for the determination of the higher fatty acids. It proved to be possible to separate the fatty acids up to C_{18} on the same column used for the C_4-C_{10} separation, but a very long column (about 50 cm long) was necessary, especially for the separation of C_{18} and C_{16} acids. Moreover, the higher acids proved to be too weak to give a distinct colour change with bromocresol green, an indicator changing its colour between pH 3.8 and pH 5.4. We therefore tried indicators with a colour change at a higher pH. Bromothymol blue (pH colour change interval 6.0-7.6) fully answered our expectations. On a silica gel column, tinted with bromothymol blue, the colour change with the higher fatty acids is very sensitive. In a tube of 6 mm internal diameter even amounts as small as 0.1 mg of each acid (about 0.0003-0.0005 mg eq.) give clearly visible bands.

With the use of bromothymol blue a second, very important advantage was reached. In preparing a column impregnated with an indicator, enough ammonia must be added to obtain the intermediate colour of the added indicator. Using bromothymol blue this amount of ammonia is about 20 times as high as is the case for bromocresol green. With this relatively high amount of ammonia as a part of the system, salt formation with the acids travelling through is very probable, causing considerable modification of the partition coefficients. In consequence of these altered partition coefficients it appeared that a column length of about 9 cm is sufficient to obtain a quick and quantitative separation of the straight-chain saturated fatty acids from C_{10} to C_{24}.

It should be emphasized that, as far as we know, these results are only possible with the especially prepared silicagel used in our work. The method of preparation of this gel, described in our earlier publication[1], was slightly modified. Therefore it seems useful to repeat this method of preparation.

PREPARATION OF SILICAGEL

To 200 ml of commercial waterglass (s.g. 1.35) 400 ml of water, some drops of methyl orange solution and, while stirring, 10*N* HCl is added until the mixture remains pink during at least 15 minutes. Then the resulting porridge is rubbed in a mortar in order to break up the lumps, after which more 10*N* HCl is added until acid to thymol blue paper. The silicic acid is then transferred to a Büchner funnel and washed with water to remove most of the HCl. Next the wet gel is suspended in about 400 ml ± 2% HCl and this suspension must stay at room temperature for 15-20 hours. Subsequently the gel is filtered again on a Büchner funnel and washed with distilled water, without allowing the precipitate to crack. The washing is continued until the filtrate is completely Cl-free. It is recommended to add the washing water automatically during this washing process (see Fig. 1). If the gel is mixed with each new portion of washing liquid, a much larger quantity of washing liquid must be used.

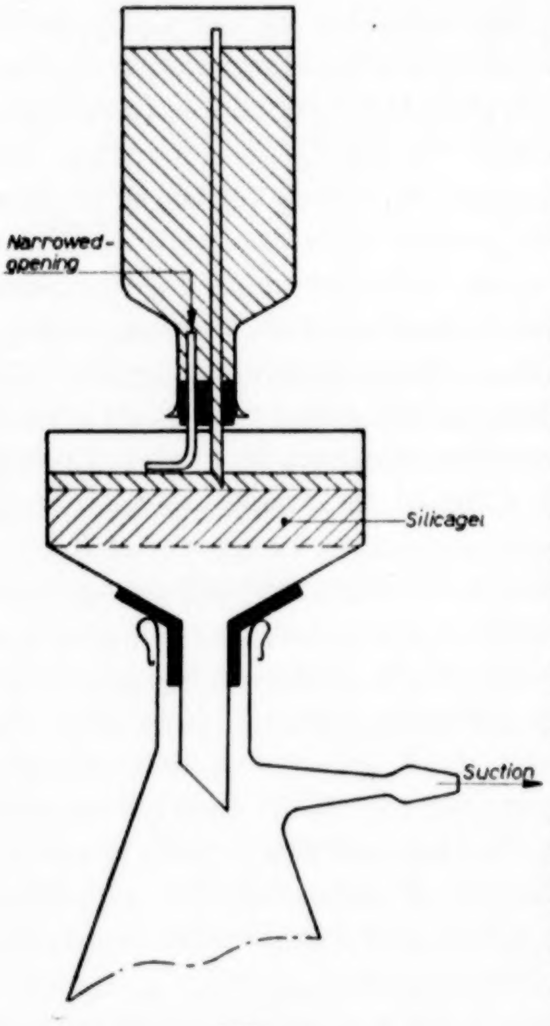

Fig. 1

After washing until acid-free, the water of the drained gel is removed by washing with 96% ethyl alcohol, again preferrably with automatic addition of the alcohol. This washing process can easily be controlled by estimating occasionally the ethanol percentage of a small portion of the filtrate from its refractive index. The first 300-400 ml of filtrate contains only very small amounts of alcohol; then the alcohol percentage of the filtrate quickly increases. The washing is continued until the alcohol percentage is about 95%, thus nearly equal to that of the washing liquid. About 1000 ml of alcohol is necessary for this washing.

It may be noted that the filtration time can be reduced markedly by inserting between the filter paper and the surface of the Büchner funnel a circular sheet of fine wire cloth or of silk cloth with a diameter somewhat smaller than the diameter of the filter paper.

After washing with alcohol the gel is dried, first at about 80° C, then at about 110° C for some hours. In order to powder small lumps, the dry gel is then lightly rubbed through a metal sieve and next dried at 150° C until constant weight. The gel, which is very hygroscopic, must be stored in a well closed vessel.

REAGENTS

1. *Silicagel.* Prepare silicic acid as described.
2. *Methanol A.R.* If not free of acid distil after shaking with some calcium oxide.

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3. Iso*octane* (2,2,4-trimethylpentane) *solvent.* Wash with alkali, then with water. Dry with anhydrous Na_2SO_4, distil and shake with excess methanol, which contains 5% of water. For this saturation use about 30 ml 95% methanol per liter *iso*octane.

In regenerating used *iso*octane, wash several times with a solution containing about 85% water, 15% alcohol and some alkali. This washing is continued until all phenolphthalein originating from the titrations is removed. Next wash out many times with water in order to remove all ethanol. Then the *iso*octane is boiled for ½ hour with some $KMnO_4$-soln. 5% (reflux condenser). After removal of the $KMnO_4$ soln., the *iso*octane is washed with water, dried with Na_2SO_4 and distilled.

If the fresh *iso*octane is not sufficiently pure, apply this regenerating procedure to the fresh *iso*octane.

4. *Ammonium hydroxide solution.* Dilute about 1 ml of 25% ammonia with 50 ml of methanol to make a solution of 0.25*N*. Control the titer of this solution from time to time.

5. *Phenolphthalein solution.* Dissolve 1 g of phenolphthalein in 100 ml of absolute alcohol and neutralize with sodium ethylate.

6. *Bromothymol blue solution.* Dissolve 250 mg of bromothymol blue in 50 ml of methanol. Add sufficient ammonium hydroxide solution to obtain a blue colour.

7. *Sodium ethylate.* Dissolve sufficient metallic sodium in aldehyde-free absolute alcohol to produce a 1-2*N* solution. Prepare a standard 0.005-0.006*N* solution by diluting a small quantity of the 1-2*N* solution with absolute alcohol. This dilute standard solution should be standardized daily.

PROCEDURE

Preparation of the chromatographic column

Working out this chromatographic method, we were mostly interested in the determination of very small quantities of acids. We therefore used rather narrow chromatographic tubes and small amounts of gel in the preparation of the columns. In general we used only 400 mg of silicagel and glass tubes with 6 mm internal diameter and 25 cm length. These tubes are somewhat narrowed at one end. The silicagel column is prepared in the following manner:

400 mg of dry silicagel, prepared as described above, is mixed in a mortar with 0.04 ml of water and 0.05 ml bromothymol blue solution during 3 minutes. Next 1.0 ml of the 0.25*N* ammonium hydroxide solution and about 0.35 ml of methanol is added and mixed well during 1 to 2 minutes. The mixture must be bluish green now and slightly moist and sticky. (For further directions concerning the just amount of methanol: see below). Subsequently the powder is mixed with

some *iso*octane solvent, rubbed for some moments to obtain a finely divided slurry. This slurry is transferred to the chromatographic tube, which is closed at the constricted end with a small cotton wool plug. To remove any air bubbles the contents of the tube are stirred with a thin glassrod. Then the top of the tube is connected with a suitable N_2-pressure source and a pressure of about 30 cm mercury is applied, which causes the gel to pack down rapidly. The pressure is released at the moment the *iso*octane solvent has sunk into the gel. The column, which must be dark green in colour, is 8.5 to 9 cm long.

The flow rate of the column should be between certain limits. This flow rate depends upon the amount of methanol used in preparing the column. The most suitable amount differs somewhat from one batch of gel to another. The right amount of methanol to be added is quickly learned by experience. If the added amount of methanol is too small, the flow rate of the column will be low and, though the separation is very good, the analysis will be more time-consuming than necessary. If the added amount of methanol is too large, the column does not pack down firmly and has a tendency to crack; in this case the flow rate will be very high. Applying a pressure of 30 cm mercury, the flow rate of the column should be between 0.7 and 1.2 ml per minute, corresponding with 10 drops in 15 to 25 seconds.

Determination and identification

The mixture of acids to be analysed is dissolved in *iso*octane solvent. A certain amount of this solution, preferably not exceeding 0.5 ml and containing no more than about 0.5 mg of the acids C_{10}-C_{18} each and no more than about 0.25 mg of the acids C_{20}-C_{24} each is pipetted on to the column and a N_2-pressure is applied until this solution has sunk into the column. Add a small portion of *iso*octane solvent and renew the pressure until this wash solvent has sunk into the gel and repeat this washing. Next the tube is partially filled up with *iso*octane solvent, the upper end of the tube is connected with a container filled with *iso*octane solvent an da pressure of 30 cm mercury is applied on this *iso*octane solvent. The reservoir can be a 250 ml boiling flask or any other suitable container, closed with a doublebored rubber stopper. This rubber stopper holds two glass tubes, one tube connecting the space above the *iso*octane solvent with the N_2-pressure source and the other tube leading the *iso*octane solvent from the reservoir to the chromatographic tube. This second tube and the chromatographic tube can be connected with a short piece of thick-walled rubber tubing.

Because of the differing partition coefficients of the fatty acids C_{10}-C_{24} between *iso*octane and methanolic ammonia solution, the individual acids pass through the column with different velocities, increasing from capric to lignoceric acid. The colour change of the bromothymol blue impregnated in the gel, indicates the position of the acids. The quantity of eluate collected while a certain band is moving from the top of the column to the bottom is called "threshold volume". If the conditions of the columns are always the same (same quantity of gel, water, methanol, ammonia, same diameter of the tubes), these threshold volumes are characteristic for each individual acid and thus, measuring the threshold volumes enables the acids to be identified. In this respect special attention should be paid to the amount of ammonia used in the preparation of the column. To obtain a column which is dark green in colour an amount of methanolic ammonia solution can be used varying from about 0.8 to about 1.2 ml 0.25*N*. The threshold volumes however depend upon the used quantity of ammonia. In Table I a number of threshold volumes is given for different quantities of ammonia. A quantity of 1.0 ml of 0.25*N* ammonia solution must be considered a suitable amount. Using this quantity all acids, the highest acids inclusive, are quantitatively separated. In order to use the threshold volumes for identification purposes, it is necessary to know exactly the titer of the ammonia solution and to add always the same quantity of ammonia.

TABLE I

INFLUENCE OF THE AMOUNT OF AMMONIA UPON THE THRESHOLD VOLUMES

Acid	Threshold volumes methanolic ammonia soln. 0.25*N* 0.90 ml	 1.00 ml	 1.10 ml
Lignoceric	3.4 ml	3.7 ml	4.0 ml
Behenic	4.2 ml	4.5 ml	5.1 ml
Arachidic	5.8 ml	6.5 ml	7.2 ml
Stearic	8.6 ml	9.8 ml	11.5 ml
Palmitic	14 ml	16 ml	19 ml
Myristic	25 ml	28 ml	34 ml
Lauric	45 ml	50 ml	57 ml
Capric	72 ml	77 ml	85 ml

Since the threshold volumes vary to a certain extent with the concentration of the acids, in exceptional cases doubt may arise about the identity of one or more acids of an unknown mixture. The following procedure enables a reliable identification: After the development of the unknown mixture the threshold volumes and the titration figures of all acids are known. If a further identification is desirable, pipette the same solution again on to the column together with a solution of a known acid (or solutions of 2 or 3 known acids) and proceed to develop the chromatogram for the second time. Comparison of the threshold volumes and the titration figures of this second development with those of the first one, shows the position(s) of the added known acid(s) among the acids to be identified. Practically in all cases it is sufficient for the identification of all acids in the mixture to know with certainty the identity of one or two acids.

After passing through the column the acid of each band is collected and titrated.

Since the maximum quantities of acid of each band are very small, it is necessary to titrate as accurate as possible. It showed that titration with 0.005*N* sodium-ethylate, using phenolphthalein as the indicator, can be performed with an accuracy of 0.01 ml on the following two conditions:

a) the titration must be done in a CO_2-free atmosphere (N_2-stream for instance).

b) the volume of the solution to be titrated must be small, preferrably no more than 2 to 3 ml. If a mixture of C_{10}-C_{24} acids are separated on the column, the highest acids (C_{24}, C_{22} and C_{20}) are completely collected in very small portions of percolate so that the titrations of these acids can be performed directly in a N_2-stream. For the acids C_{18}-C_{10} increasing volumes of *iso*octane solvent are required to collect completely the acid of each band (from C_{18} to C_{10} increasing from about 6 ml to about 40 ml). To obtain the desirable small volume we reduced the percolate portion of each acid in the following manner: a few particles of powdered, acid-free lapis pumicis are added and most of the *iso*octane solvent is distilled off in a glycerin-water bath at a temperature of about 115° C, the last part of the distillation taking place in a glass tube about 8 × 1.5 cm with marks at 2 and 3 ml. This distillation is continued until a volume of 2 ml is reached. After cooling and addition of a drop of phenolphthalein solution the solution is titrated in a N_2-stream with 0.005*N* sodium ethylate. A corresponding blank, though very small, must be subtracted.

Since the lower acids of this series are more or less volatile, it might be expected that the distillation process might cause small losses. Therefore this point was especially investigated with capric acid, the most volatile acid of this series (boiling point 268° C). It showed that even with quantities of capric acid 10 times as large as used in the analyses no loss at all could be detected. Thus this simple and quick concentrating method can be considered fully reliable.

If the flow rate is normal (about 1 ml/min), the separation and determination of a complete mixture of C_{10}-C_{24} acids can easily be accomplished in 2½ to 3 hours. The concentration of the larger percolate portions can be performed for the most part during the development.

RESULTS AND DISCUSSION

The results obtained with this method were highly satisfactory, the bands, even of minor amounts of acid, are very distinct and during development the different acids of the mixture are quickly separated. However, attention must be paid to the fact that the quantities of the acids to be separated should not exceed a certain limit. That this limit is low is mainly due to the high sensitivity of the colour change with bromothymol blue. This sensitivity is so high that on a column of 400 mg gel even amounts of acid as small as 0.0003 mg eq. (less than 0.1 mg of acid) give visible bands. In consequence of this high sensitivity the hindmost part of the band, though yellow tinted, contains only negligible amounts of acid. If the used quantities of acid are too high, the faintly yellow tail of the band will reach until the following band, thus disturbing a distinctly visible separation. For a 400 mg column the maximal quantities of the C_{10}-C_{18} acids should be about 0.003 mg eq. per acid and of the C_{20}-C_{24} acids about 0.0015 mg eq. per acid. The method proved to be extremely suitable for the separation and determination of these semimicro amounts. For the analyses of larger quantities longer or wider columns and more silicagel must be used.

Since the indicator bromothymol blue is very sensitive even for small amounts of weak acids, *iso*octane solvent containing atmospheric CO_2 will cause gradually a small yellow band in the top of the column. This does not cause any interference.

Table II shows the recoveries of even-chained saturated acids in C_{10}-C_{18} mixtures (Table II A-E), in C_{18}-C_{20} mixtures (Table II F-H) and in C_{18}-C_{24} mixtures (Table II I-J). The results of Table II, which were obtained partly on 400 mg columns and partly on columns of 1000 mg gel in 9.5 mm tubes, show that recoveries are within 5%. (Some amounts we considered too small for a recovery evaluation.)

TABLE II

RECOVERY OF ACIDS FROM MIXTURES

Acid	Amount taken (ml 0.005N)	Amount determined (ml 0.005N)	Recovered (%)
Mixture A			
Stearic	1.65	1.61	98
Palmitic	1.41	1.46	104
Myristic	1.88	1.92	102
Lauric	1.59	1.61	101
Capric	1.96	2.01	103
Mixture B			
Stearic	2.32	2.23	96
Palmitic	2.02	2.06	102
Myristic	1.96	2.04	104
Lauric	1.71	1.73	101
Capric	2.11	2.08	99
Mixture C			
Stearic	1.36	1.33	98
Palmitic	1.13	1.18	104
Myristic	1.07	1.10	103
Lauric	0.98	1.03	105
Capric	1.17	1.22	104
Mixture D			
Stearic	0.68	0.70	103
Palmitic	0.61	0.62	102
Myristic	0.63	0.64	102
Lauric	0.58	0.61	105
Capric	0.59	0.60	102

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Mixture E			
Stearic	0.47	0.49	104
Palmitic	0.20	0.20	
Myristic	0.49	0.48	98
Lauric	0.20	0.19	
Capric	0.53	0.51	96
Mixture F			
Arachidic	0.52	0.50	96
Stearic	0.63	0.62	98
Mixture G			
Arachidic	0.26	0.26	
Stearic	1.22	1.20	98
Mixture H			
Arachidic	0.13	0.14	
Stearic	1.22	1.19	98
Mixture I			
Lignoceric	0.09	0.08	
Behenic	0.14	0.15	
Arachidic	0.31	0.33	
Stearic	0.77	0.74	96
Mixture J			
Lignoceric	0.36	0.34	94
Behenic	0.69	0.67	97
Arachidic	0.65	0.68	105
Stearic	1.09	1.11	102

As is mentioned above the threshold volumes vary to a certain extent with the concentration of the acids: the smaller the concentration the slower the band moves through the column. Therefore the most difficult separation is the separation of a small quantity of an acid from a normal amount of its nearest even-numbered lower homologue (Table II G and H). Even if the ratio of both acids is between 1:10 and 1:20 the separation is virtually quantitative. If the ratio is still more unfavourable, a longer column must be used for a quantitative seperation or in a first passage the small first band must be collected together with the first part of the following band, and, after concentrating the percolate fraction, this mixture must be transferred again on a column. Since the ratio between the two acids is more favourable now, in this second passage the first band can easily be separated and determined quantitatively.

The composition of the mobile phase needs an explication. The *iso*octane solvent must be in equilibrium with the immobile phase. If the mobile phase is saturated with methanol 100%, part of the dissolved methanol will separate in the column, because of the presence of some water in the immobile phase; this excess of methanol dissolves the indicator, causing a gradual discolouring, beginning at the top. If the methanol used for saturation of the *iso*octane, contains too much water, the quantity of methanol dissolving in the *iso*octane is too low and consequently the column becomes gradually slightly transparent. The water-percentage of the methanol, used for the saturation of the mobile phase, should be chosen so that the appearance of the column does not alter during development. This water content of the methanol is not very critical. About 30 ml of methanol 95% for the saturation of 1 liter of *iso*octane proved to be suitable.

Just as in the methods of RAMSEY AND PATTERSON[3] and of BOLDINGH[4], the naturally occurring unsaturated fatty acids, such as oleic, linoleic and linolenic acid, do interfere and must be removed by suitable means before the method can be applied to the separation of the straight-chain saturated fatty acids.

Some remarks about the separation of the lower fatty acids

It is possible now to determine the fatty acids C_2-C_{24} chromatographically using silicagel columns tinted with an indicator. In 1948 we published (in Dutch)[5] a modification of the method of ELSDEN[6] for the separation of the lower fatty acids C_2-C_4. During that work a silicagel prepared according to GORDON, MARTIN AND SYNGE[7] was used. Afterwards it showed that the gel prepared as described above was a much better carrier for this separation. The new gel has a higher capacity for water (immobile phase), the separation is better, the colour change is more sensitive and the bands are sharper. Using the new gel the acids C_2, C_3, C_4, C_5 and C_6 can quantitatively be separated on a column of only 4 to 5 cm length. In preparing this column, mix 300 mg of gel with: 0.06 ml bromocresol green solution 0.4%, 0.35 to 0.40 ml of water, about 0.10 ml of NaOH 0.1*N*; make a slurry with some TB_6 (CCl_4 with 6% butanol) and pour in a tube 6 mm internal diameter; apply pressure of 30 cm mercury. Mobile phase is TB_6. Suitable quantities of acids: 0.002-0.01 mg eq. per acid.

Our publication in 1951[1] concerned the volatile acids C_4 through C_{10}. We then were not interested in C_{12}. Our later experiments showed that for this column the range of usefulness can be extended to C_{12}, so that C_{10} and C_{12} can be determined either on this column or on the column impregnated with bromothymol blue; the most important difference is that these acids C_{10} and C_{12} are the most quickly moving acids on the first column and the slowest ones (and the most time-consuming) on the bromothymol blue column. In the method for the separation of the C_4-C_{12} acids also *iso*octane solvent is used as the mobile phase and methanol with some water as the immobile phase. It should be accentuated now that for this method too, this *iso*octane solvent must be prepared as described in this paper.

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SUMMARY

A semimicro-method based on partition chromatography is described for the determination of the saturated, straight-chain fatty acids C_{10}-C_{24}. For this method a silicagel column is used, tinted with a suitable indicator, so that each acid is distinctly visible and only one titration is required for each acid. A description is given of the preparation of a silicagel, which is highly suitable for this chromatographic analyses. Amplifying earlier publications some remarks are made concerning the separation of the lower fatty acids.

RÉSUMÉ

Une semi-micro méthode, basée sur la chromatographie de partage, est décrite pour la détermination des acides gras saturés C_{10}-C_{24} à chaines droites. On utilise une colonne de silicagel colorée avec un indicateur approprié, de sorte que la position de chaque acide est visible distinctement et une seule titration est nécessaire pour chaque acide Une description est présentée pour la préparation de silicagel, spécialement appropriée à cette analyse chromatographique. Complétant des publications antérieures, quelques indications sont données concernant la séparation des acides gras inférieurs.

ZUSAMMENFASSUNG

Eine Semimicro-Methode für die Bestimmung der gesättigten Fettsäuren C_{10}-C_{24} mit gerade Ketten, basiert auf Verteilungschromatographie, wird beschrieben. Für diese Methode wird eine Silicagel-Säule angewendet, die mit einem geeigneten Indikator gefärbt ist, sodass die Lage jeder Säure deutlich sichtbar ist und für jede Säure nur eine Titration nötig ist. Eine Beschreibung wird gegeben von der Darstellung eines Silicagels, der für diese chromatographische Analyse sehr geeignet ist. Zur Ergänzung früherer Veröffentlichungen werden einige Bemerkungen über die Trennung der niederen Fettsäuren gemacht.

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HETEROMETRIC MICROTITRATION OF COPPER WITH OXINE

by

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The heterometric determination of copper with oxine is a very sensitive method which ranks in accuracy with the heterometric determination of nickel with dimethylglyoxime. Quantities of a few tenths of a mg of copper in 20 ml solutions can be titrated with an accuracy of a few tenths of a microgram per ml. The lower limit of copper concentration which can be determined is approximately 0.0004 mole since a saturated copper oxinate solution, at room temperature, may have a concentration of about 0.0001 mole. Under normal conditions, the titration takes 10-15 minutes. In a separate report it will be shown that our method is especially suitable for the direct determination of copper in the presence of large excesses of other metals without separation of the metals. This method may be used for the standardisation of alcoholic solutions of oxine.

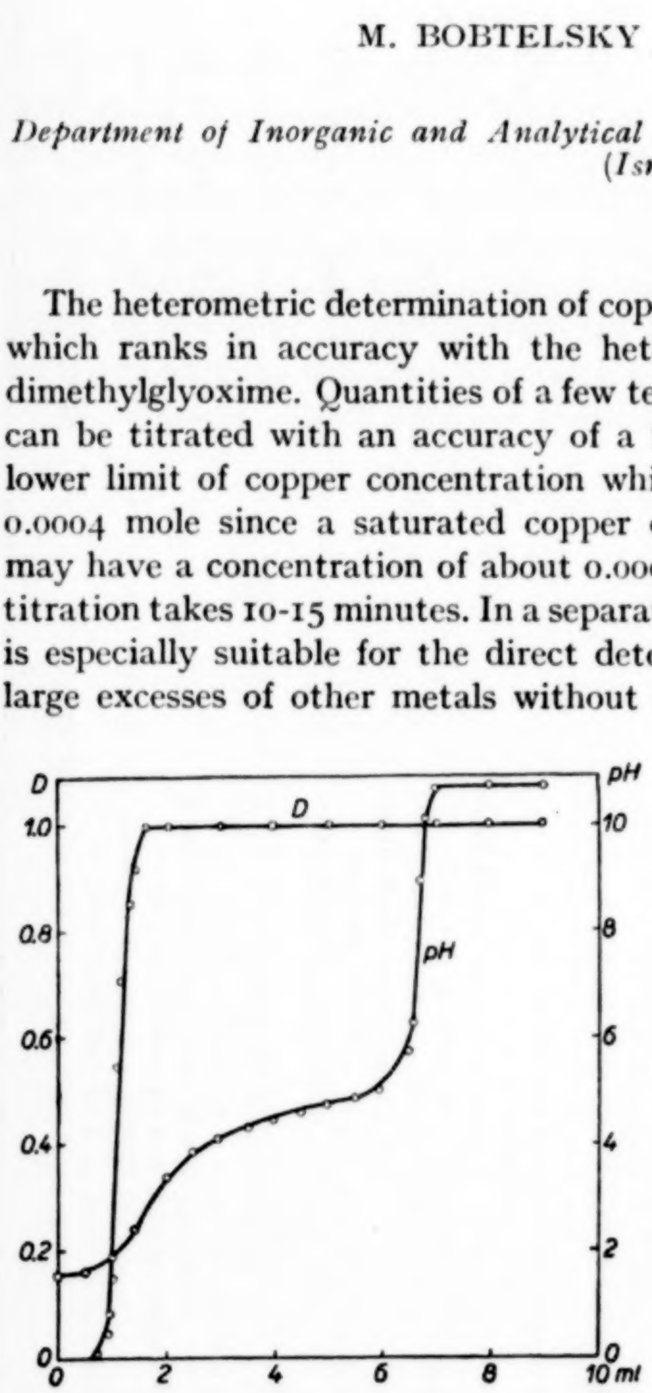

Fig. 1. Composition: 5 ml 0.01M $Cu(NO_3)_2$ + 5 ml 0.02M Oxine/50% alc. + 1 ml 1.0 M HCl + 5 ml 1.0M CH_3COOH + 24 ml H_2O + X ml 1.0M NaOH.

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TECHNIQUE

The same apparatus and the same technique were used as in previous reports[1-5]. The point on the abscissa of the first maximum of the optical density was determined in the following way: the titration curve in the vicinity of the endpoint was enlarged and a line was drawn through the maxima points obtained. The intersection of this line with the last portion of the density curve gave the endpoint of the titration. All measurements were made with an orange filter.

TABLE I

General Composition: 5 ml aM $Cu(NO_3)_2$ + 15 ml supplementary + x ml bM Oxine 50% alc. Temp. = 18-22°.

Exper. number	Composition	x ml		Cu mg	Error		Maxim. optical density	Initial precipit. at ml	Titration time in min.
		calcul.	found	present	micrograms	γml			
1	5 ml 0.005M $Cu(NO_3)_2$ + 3 ml 1.0M Na acet + 12 ml H_2O + x ml 0.02M Oxine	2.5	2.48	1.589	—12.7	—0.6	1.17	0.2	13
2	5 ml 0.005M $Cu(NO_3)_2$ + 3 ml 1.0M Na acet + 8 ml H_2O + 4 ml alc + x ml 0.02M Oxine	2.5	2.50	1.589	0.0	0.0	1.17	0.2	7
3	5 ml 0.002M $Cu(NO_3)_2$ + 3 ml 1.0M Na acet + 8 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	1.98	0.6356	— 6.4	—0.3	0.81	1.0	12
4	5 ml 0.002M $Cu(NO_3)_2$ + 1 ml 1.0M CH_3COOH + 10 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	2.07	0.6356	+22.2	+1.1	0.66	1.8	21
5	5 ml 0.001M $Cu(NO_3)_2$ + 3 ml 1.0M Na acet + 8 ml H_2O + 4 ml alc + x ml 0.005M Oxine	2.0	1.98	0.3178	—3.2	—0.15	0.54	1.6	8
6	5 ml 0.001M $Cu(NO_3)_2$ + 1 ml 1.0M Na acet + 1 ml 1.0M CH_3COOH + 9 ml H_2O + 4 ml alc + x ml 0.005M Oxine	2.0	2.12	0.3178	+19.1	+1.0	0.54	1.4	18
7	5 ml 0.002M $Cu(NO_3)_2$ + 1 ml 1.0M Na acet + 1 ml 1.0M CH_3COOH + 9 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	2.0	0.6356	0.0	0.0	0.85	0.8	13
8	5 ml 0.002M $Cu(NO_3)_2$ + 5 ml 0.1M KH Phthalate + 6 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	2.03	0.6356	+9.5	+0.5	0.82	1.0	9
9	5 ml 0.002M $Cu(NO_3)_2$ + 15 ml H_2O + x ml 0.01M Oxine	2.0	1.98	0.6356	—6.4	—0.3	0.40	0.6	20
10	5 ml 0.002M $Cu(No_3)_2$ + 1 ml 1.0M K_2 Tartrate + 10 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	1.98	0.6356	—6.4	—0.3	0.82	1.0	11
11	5 ml 0.002M $Cu(NO_3)_2$ + 2 ml 1.0M K_2 Tartrate + 2 ml 1.0M NH_4OH + 7 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	2.02	0.6356	+6.4	+0.3	0.85	1.4	21
12	5 ml 0.002M $Cu(NO_3)_2$ + 2 ml 1.0M Na_3 Citrate + Citrate + 11 ml H_2O + 4 ml alc + x ml 0.01M Oxine	2.0	2.02	0.6356	+6.4	+0.3	0.76	0.8	10

REAGENTS

All reagents used were either analytical reagents or chemically pure. The 50% alcoholic oxine solution was prepared by diluting an alcoholic solution of oxine with water.

RESULTS

Fig. 1 presents the results of two parallel heterometric and pH-titrations carried out in a special vessel. The curves show the dependence of the precipitation of copper oxinate on the pH. The quantitative precipitation occurs at pH ∿ 3.0 and no further influence of the rising pH on the precipitate is observed.

Fig. 2 presents a series of optical density curves (the numbers are the same as in Table I) which were obtained by a dropwise addition of 50% alcoholic solutions of oxine to copper solutions of known concentrations. In all cases a saturated solution of copper oxinate ($CuOx_2$) is obtained first. At a certain point on the abscissa, which depends on the composition of the solution, the initial

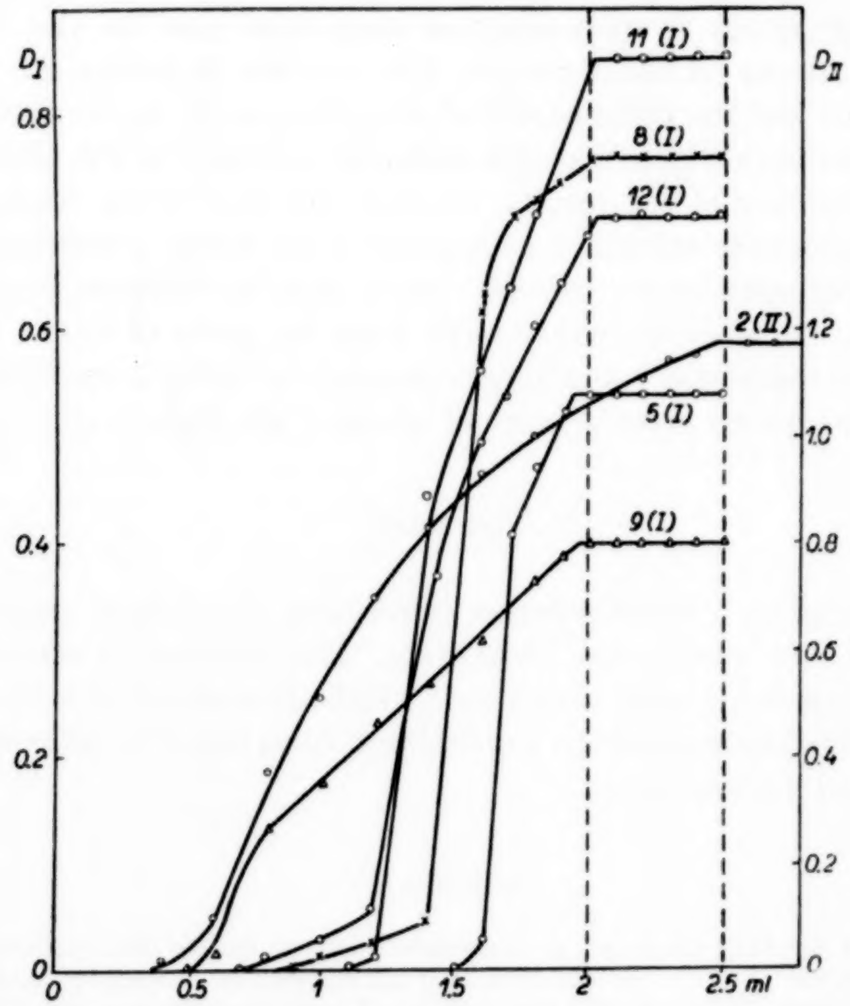

Fig. 2. Titration curves of copper nitrate with oxine

precipitation occurs: the optical density rises until the first point of the maximum optical density is reached. At this critical point the precipitation is completed. Table I gives a compilation of the composition and the results of a series of heterometric titrations, made with the purpose of studying the influence of various reagents on the results. Experiments 1 and 2 differ only by the presence of alcohol in exp. 2. In both cases Na-acetate was added. Although similar results were obtained, the readings in exp. 1 are less certain and take more time. Subsequent titrations were therefore made in the presence of alcohol. If we compare experiments 2, 3 and 5 we see that the maxima optical density values obtained are not proportionate to the content of copper. The point of initial precipitation shifts nearer to the endpoint of the titration the more dilute the analysed copper solution becomes. Free acetic acid may partly dissolve the precipitate (exp. 4). In buffered acetate solutions the readings are less certain in dilute solutions of copper (exp. 6) but the buffer is harmless in more concentrated copper solutions (exp. 7). Exp. 9 carried out in absence of alcohol and acetate proceeds with difficulties: the titration time is longer although the precipitation begins earlier. KH phthalate may well be used as a buffer instead of Na-acetate (exp. 8). Of special interest are the titrations which were carried out in the presence of tartrate or citrate (exps. 10-12) as such solutions were used later for the determination of copper in presence of other metals. The maxima densities are almost equal in all three cases but the point of initial precipitation is, in the presence of NH_3, shifted nearer to the endpoint, as the solubility is higher in the alkaline solution.

As to the accuracy of the results, we may say that under normal conditions (see method below) the error is 0.0-0.5 γ per 1 ml. Using a somewhat more concentrated copper solution the density curve may be widened (exp. 2) and the endpoint of the titration is further away from the point of initial precipitation. In this case the maximum value may be lowered by using a vessel of larger diameter (= 5.0 cm) which gives a layer of about 1 cm high.

METHOD

To about 15 ml of a water solution containing $\gtrless$ 1 mg of copper, are added 2-4 ml alcohol and 2 ml 1.0M Na-acetate. The solution is stirred intensively and titrated heterometrically with a 50% alcoholic solution of 0.01-0.02M oxine. The latter is added dropwise from a microburet (0.01 ml). The endpoint is obtained from the optical density curve.

SUMMARY

A new heterometric method is presented for a quick micro-determination of copper with oxine. A few tenths of a mg of copper in 20 ml of solution may be determined with an accuracy of a few tenths of a microgram per ml. The determination is made at room temperature and takes 10—15 minutes.

RÉSUMÉ

Une méthode hétérométrique est présentée pour la microdétermination rapide du cuivre avec l'oxine. Quelques dixièmes de mg de cuivre peuvent être dosés avec une précision de quelques dixièmes de microgram par ml. La détermination est réalisée à la température ordinaire et dure 10—15 minutes.

ZUSAMMENFASSUNG

Eine heterometrische Methode zur raschen Mikrobestimmung von Kupfer mit Oxine wird presentiert. Wenige Zehntel mg Kupfer in 20 ml Lösung können mit einer Genauigkeit von Zehntel Mikrogramm per ml bestimmt werden. Die Bestimmung dauert bei gewöhnlicher Temperatur 10—15 Minuten.

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DIRECT HETEROMETRIC MICROTITRATION OF COPPER WITH OXINE IN THE PRESENCE OF OTHER METALS

by

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INTRODUCTION

In a previous report a method was presented for a quick heterometric determination of micro quantities of copper with oxine in the absence of interfering cations. This report deals with the determination of copper in the presence of an excess of other metals. It was intended to investigate whether a direct determination of copper may be carried out in the presence of complex binders such as tartrate or citrate.

The amount of copper in the solutions analysed is about $\gtrless$ 1 mg and is about 5% of the total in the presence of the light metals Mg and Al, about 2% in the presence of other metals such as Zn, Mn, Co, Ni, Cd and Cr and about 0.2% in the presence of Pb. This investigation is in no way complete. Further investigation will show to what extent the concentration of the citrate or tartrate and consequently of the metals present, may be increased without interfering with the determination of the copper. Only in the case of iron did we not succeed in obtaining a clear endpoint (no maximum was obtained). The time required for a complete titration is 10-20 minutes and the error is 0-1.0 γ/ml.

No interference due to adsorption, which would shift the endpoint of the titration, was noticed. This conforms with the results of heterometric investigations in general. This may be explained by the fact that the *primary* particles which form the suspension generally do not adsorb. On the other hand, the point of *initial* precipitation is postponed in many cases, especially in more dilute copper solutions, by the presence of an excess of certain metals (in complex form). The latter may be explained by the influence of the metal complexes on the solubility of copper oxinate or it may be caused by supersaturation. In a somewhat higher concentration of copper this phenomenon disappears. The position of the initial point, however, is without influence on the endpoint of the titrations.

TECHNIQUE

All the titrations were made with a heterometer (photometer for the titration of suspensions). Generally a cylindrical vessel was used which had an inner diameter of 3.8 cm. Titrations number 4, 11 and 12 were made in a vessel of diameter 5.0 cm in order to decrease the optical density. In all titrations with oxine a deep orange filter was used. Only the solutions containing iron or cobalt were titrated with a red filter. No additional filters were required in the presence of other coloured salts as the colour of the salt solution did not change during the titrations. A microburet (0.01 ml) was used. The maximum density point was obtained from enlarged curves. A line was drawn through the maximum points obtained and the point of intersection of this line with the last portion of the density curve was taken as the endpoint of the titration. In some cases where a convex optical density curve was obtained, the first contact point of the density curve with the maximum density line was taken instead.

Reagents

The reagents were either analytical reagents or chemically pure.

RESULTS

Table I presents a complication of the composition and results of titrations of copper in the presence of other metals. Figs. 1 and 2 show the course of the

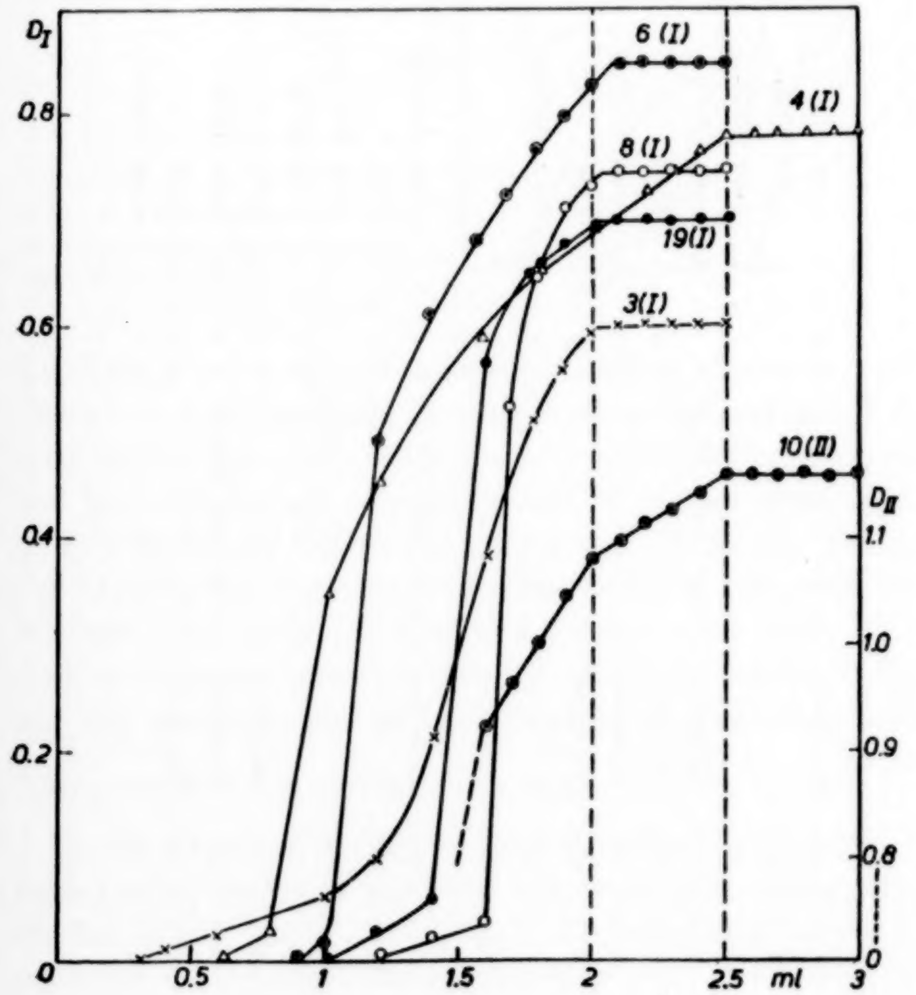

Fig. 1. Titration curves of copper in the presence of other metals.

TABLE I

GENERAL COMPOSITION: 5 ml aM $Cu(NO_3)_2$ + 6 ml Supplementary + 5 ml bM salt + 4 ml alcohol + X ml cM Oxine 50% alcohol.

(5 ml 0.002M $Cu(NO_3)_2$ = 0.6356 mg Cu)
(5 ml 0.005M ,, = 1.589 mg Cu)

Temp. 16°—24° C

Exper. number	Supplementary	Cu $(NO_3)_2$ molar	Salt			x found ml	Error		Max. optical density	Initial precip. at ml	Titration time in min	Oxine molarity
			name	molarity	mg metal		γ	γ/ml				
1	2 ml 1.0M K_2-tartrate + 2 ml 1.0M NH_4OH + 2 ml H_2O	0.002	H_2O	—	—	2.05	+15.9	+0.8	0.85	1.4	7	0.01
2	2 ,, 1.0,, Na_3-citrate — + 4 ,, ,,	0.002	,,	—	—	2.02	+6.4	+0.3	0.76	0.8	10	0.01
3	2 ,, 1.0,, ,, — + 4 ,, ,,	0.002	$MgCl_2$	0.1	12.2	2.02	+6.4	+0.3	0.60	1.0	16	0.01
4	2 ,, 1.0,, ,, + 4 ,, ,,	0.005	$Zn(NO_3)_2$	0.1	32.7	2.50	0.0	0.0	0.78*	0.8	10	0.02
5	2 ,, 1.0,, K_2-tartrate + 2 ml 1.0M NH_4OH + 2 ,, ,,	0.002	$MnCl_2$	0.1	27.5	2.06	+19.1	+1.0	0.65	0.4	22	0.01
6	2 ,, 1.0,, Na_3-citrate + 4 ,, ,,	0.002	,,	0.1	—	2.07	+22.3	+1.1	0.85	1.2	17	0.01
7	2 ,, 1.0,, K_2-tartrate + 4 ,, ,,	0.002	$Co(NO_3)_2$	0.1	29.5	2.13	+41.4	+2.1	0.85	1.3	10	0.01
8	2 ,, 1.0,, Na_3-citrate + 4 ,, ,,	0.002	,,	0.1	—	2.03	+9.5	+0.5	0.75	1.6	10	0.01
9	2 ,, 1.0,, ,, + 4 ,, ,,	0.002	$Ni(NO_3)_2$	0.1	29.4	2.15	+47.6	+2.4	0.11	1.0	10d	0.01
10	2 ,, 1.0,, ,, + 4 ,, ,,	0.005	,,	0.1	—	2.50	0.0	0.0	1.16	1.0	19	0.02
11	2 ,, 1.0,, ,, + 4 ,, ,,	0.005	,,	0.1	—	2.50	0.0	0.0	0.89*	1.2	10	0.02
12	2 ,, 1.0,, K_2-tartrate + 2 ml 1.0M NH_4OH + 2 ,, ,,	0.002	$Cd(NO_3)_2$	0.05	28.1	2.00	0.0	0.0	0.21	0.2	17	0.01
13	2 ,, 1.0,, ,, + 2 ,, 1.0,, ,, + 2 ,, ,,	0.005	,,	0.05	—	2.45	−31.8	−1.6	0.78*	0.3	10	0.02
14	2 ,, 1.0,, ,, + 2 ,, 1.0,, ,, + 2 ,, ,,	0.002	$Pb(NO_3)_2$	0.1	103.6	2.03	+9.5	+0.5	0.51	0.8	14d	0.01
15	2 ,, 1.0,, ,, + 2 ,, 1.0 ,, ,, + 2 ,, ,,	0.002	$AlCl_3$	0.1	13.5	2.0	0.0	0.0	0.71	1.1	15d	0.01
16	2 ,, 1.0,, Na_3-citrate + 4 ,, ,,	0.002	,,	0.1	—	2.1	+31.8	+1.6	0.37	1.4	12d	0.01
17	2 ,, 1.0,, K_2-tartrate + 2 ml 1.0M NH_4OH + 2 ,, ,,	0.002	$FeCl_3$	0.1	27.9	>2.5	—	—	>0.77	1.1	—	0.01
18	2 ,, 1.0,, Na_3-citrate + 4 ,, ,,	0.002	,,	0.02	—	> 2.5	—	—	>1.0	1.2	—	0.01
19	2 ,, 1.0,, ,, + 4 ,, ,,	0.002	$Cr(NO_3)_3$	0.1	26.0	2.05	+15.9	+0.8	0.70	1.2	10	0.01

* diameter of the cylinder = 5 cm.

same titrations (the numbers of the curves correspond to the numbers of the experiments in Table I). The titrations were made either in citrate or tartrate solutions. No fundamental difference was observed in either case, although in many instances only in the presence of one of them could good results be obtained.

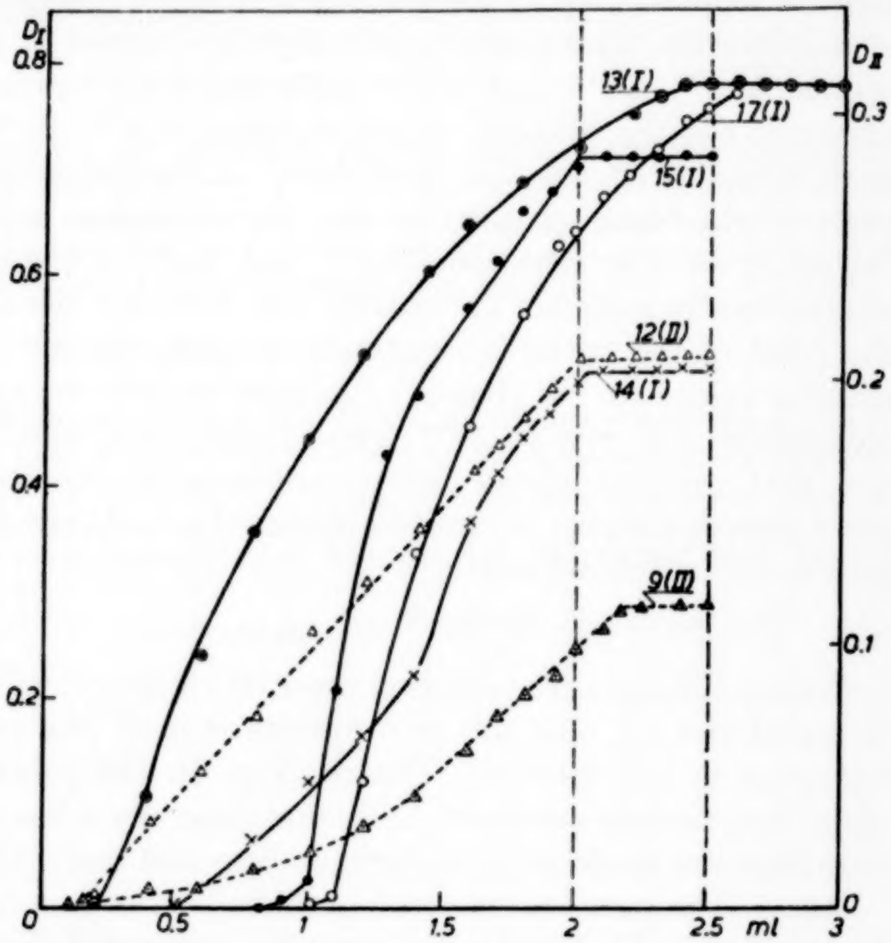

Fig. 2. Titration curves of copper in the presence of other metals.

Cd^{+2} gave a precipitation in the presence of citrate and a tartrate solution was therefore used instead; the highest concentration of Cd^{+2} used could be only 0.05 molar. In some cases (exp. 9 and 12) the maximum density values were too low and higher concentrations of copper were used instead.

The titrations which proceeded with difficulty are marked in the Table with "d". Generally, the accuracy is the same in the presence of either of the complex binders. The error lies between 0.0-1.0 γ/ml. Only in a few cases (which were not used as analytical methods) were the errors higher. The results presented are not complete and in each case further detailed investigation is required.

Some remarks concerning the results.

In the titration of copper with oxine in the presence of large excesses of other metal salts, we meet with the following difficulties: the point (on the abscissa) of the *initial* precipitation and the maximum density *value* may both change with the added salt. The former may shift very near to the end of the titration and the latter may be very depressed. These phenomena depend on the salt added and on the complex binder used. The above difficulties *may be overcome either by increasing (doubly) the amount of copper or by changing the complex binder.*

Analysing Table I we see the following: The blank in the presence of a basic tartrate solution (exp. 1) gives a point of initial precipitation at 1.4 ml or at 2/3 of the titration. This point is only slightly changed in the presence of trivalent metals. Mn^{+2}, Cd^{+2} and Pb^{+2} shift the point towards the beginning of the titration, but the maxima values obtained (Cd^{+2}, Pb^{+2}) are depressed. Even more complicated are the phenomena in the presence of citrate. The initial point of the blank (exp. 2) occurs, in comparison with tartrate, more at the beginning of the titration. Mg^{+2} and Zn^{+2} (Cd^{+2} gives a precipitate with citrate) hardly influence the results. The trivalent metals, Mn^{+2} and Co^{+2} shift the point of the initial precipitation towards the end of the titration, but the maxima values are not changed. Contrary to this, the maxima values are greatly reduced in the case of Ni^{+2} (exp. 9) and Al^{+3} (exp. 16). It is interesting to note that, using the higher copper concentration, the depression of the maximum value disappears (exp. 10) and the blank value is obtained again. These phenomena require an individual study.

METHOD

General technique. The solution must be vigorously stirred during the titration. A microburet ($\pm$ 0.01 ml) or a syringe is used (the end of the buret must be immersed in the solution). The readings on the galvanometer are taken only when they become constant: this takes generally a few seconds to a minute. The titrations are made at room temperature and last 10-20 minutes.

Alloys. The metal is dissolved in nitric acid or in a mixture of nitric acid and hydrochloric acid. Excess acid must be evaporated. The analysed solution must be neutral.

Determination of copper in the presence of sodium citrate

The solution contains an excess of Mg, Mn, Co, Ni, Al or Cr.

To 18 ml of a solution which contains $\gtrless$ 1 mg copper (as nitrate or chloride), are added 2 ml of 1.0*M* sodium citrate. The solution is titrated with 0.01*M*-0.02*M* oxine (50% alcohol). If the solution contains an excess of Zn, Al or Ni, the amount of copper must be doubled. Error 0.-1.0 γ/ml.

Determination of copper in the presence of basic potassium (or sodium) tartrate

The solution contains an excess of Al, Mn, Cd or Pb

To 16 ml of a solution which contains $\gtrless$ 1 mg copper (as nitrate or chloride), are added 2 ml of 1.0*M* potassium tartrate and 2 ml of 1.0*M* NH_3. The solution is titrated with 0.01*M*-0.02*M* oxine (50% alcohol). In the presence of an excess of Cd^{+2} the amount of copper must be doubled. Error 0-1.0 γ/ml.

SUMMARY

A new heterometric method is presented for a rapid micro-determination of copper with oxine. $\gtrless$ 1 mg of copper in 20 ml of solution may be determined with an accuracy of 0-1.0 microgram per ml. The solution may contain 95% Mg or Al, 98% Zn, Mn, Co, Ni, Cd or Cr and 99.8% Pb. The determination is made at room temperature and takes 10-20 minutes.

RÉSUMÉ

Une méthode hétérométrique est présentée pour la micro-détermination rapide du cuivre avec l'oxine. On peut doser $\gtrless$ 1 mg de cuivre dans 20 ml de solution avec une précision de 0-1.0 microgram par ml. La solution peut contenir 95% Mg ou Al, 98% Zn, Mn, Co, Ni, Cd ou Cr et 99.8% Pb. Cette détermination est faite à la température ordinaire et dure environ 10-20 minutes.

ZUSAMMENFASSUNG

Eine heterometrische Methode zur raschen Mikrobestimmung von Kupfer mit Oxine wird presentiert. $\gtrless$ 1 mg Kupfer in 20 ml Lösung kann mit einer Genauigkeit von 0-1.0 Microgramm per ml bestimmt Werden. Die zu untersuchende Lösung kann enthalten 95% Mg oder Al, 98% Zn, Mn, Co, Ni, Cd oder Cr, sowie 99.8% Pb. Die Bestimmung wird bei gewohnlicher Temperatur ausgeführt und dauert etwa 10-20 Minuten.

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PONT ÉLECTROLYTIQUE ET ÉLECTRODE DE RÉFÉRENCE POUR TITRAGES POTENTIOMÉTRIQUES

par

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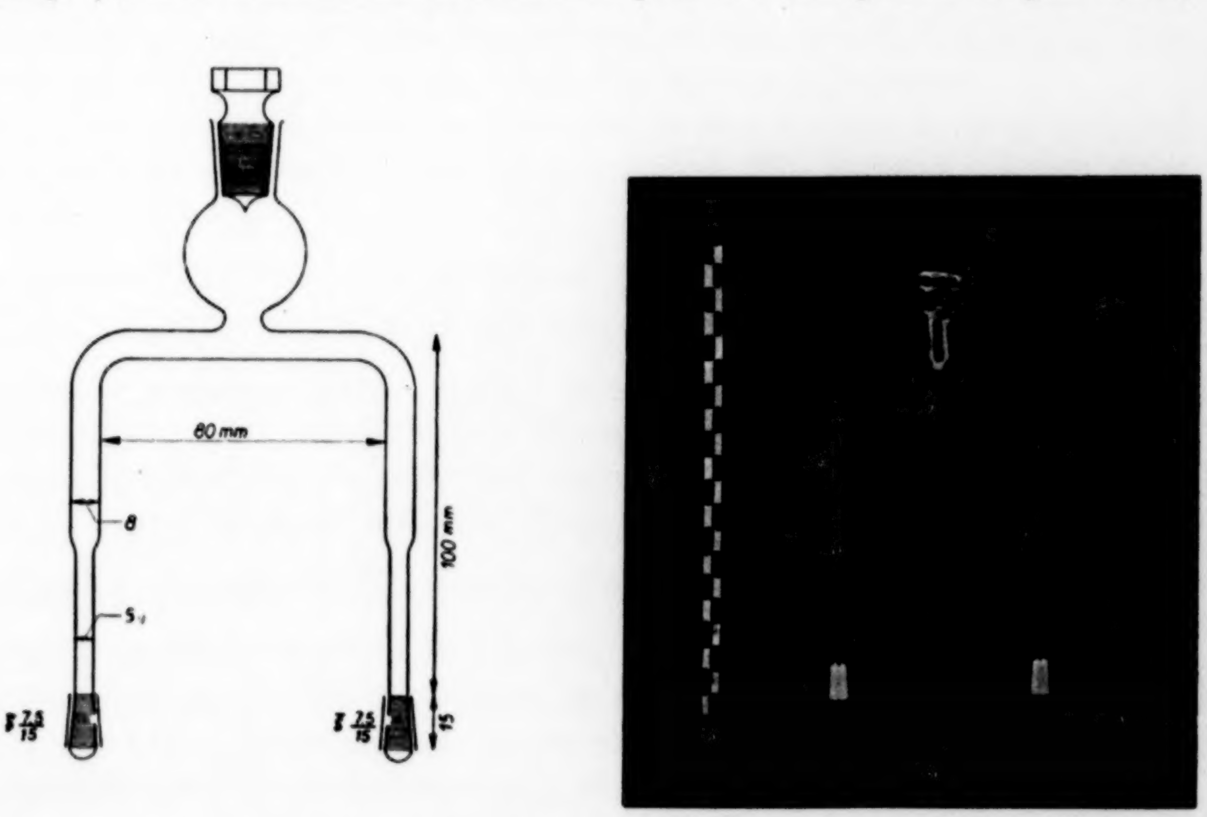
Divers types de ponts électrolytiques sont employés pour établir, lors de dosages potentiométriques, la jonction liquide entre la cellule de titrage et l'électrode de référence. Les plus simples, les ponts d'agar-agar (tubes en U remplis d'un gel d'agar-agar contenant KCl ou KNO_3) et le pont de MÜLLER[1], doivent être renouvelés souvent et ne conviennent pas pour l'analyse courante. Les ponts électrolytiques d'après DIETERLE[2] et LAITINEN[3], probablement les plus utilisés, sont fermés à leurs extrémités par de petites plaques en verre fritté de faible porosité. Ce dispositif ne supprime cependant pas complètement le siphonnage· il faut donc maintenir, surtout pour les titrages de longue durée,



a Fig. 1. Pont électrolytique. *b*

le même niveau de liquide dans tout le système. En outre, les pores du verre fritté se bouchent peu à peu lors de titrages par précipitation, de sorte que la résistance électrique du pont augmente considérablement. Il faut alors nettoyer les plaques frittées et remplir à nouveau le pont, ce qui est assez fastidieux.

LaMer et Baker[4] ont décrit un pont électrolytique obturé par des bouchons rodés, et Irving et Smith[5], un autre fermé à l'aide de baguettes rodées, insérées dans le tube. La jonction liquide s'établit par le film de solution se trouvant entre les parties rodées. Une modification de ces appareils est représentée par la Fig. 1. Les extrémités du pont portent des rodages percés (diamètre de l'orifice: env. 1 mm) sur lesquels s'adaptent des douilles rodées non percées. Ces rodages doivent être de grain fin, afin de supprimer tout siphonnage.

Pour de nombreux titrages potentiométriques, on peut cependant renoncer à l'emploi d'un pont électrolytique et utiliser des électrodes de référence qu'on

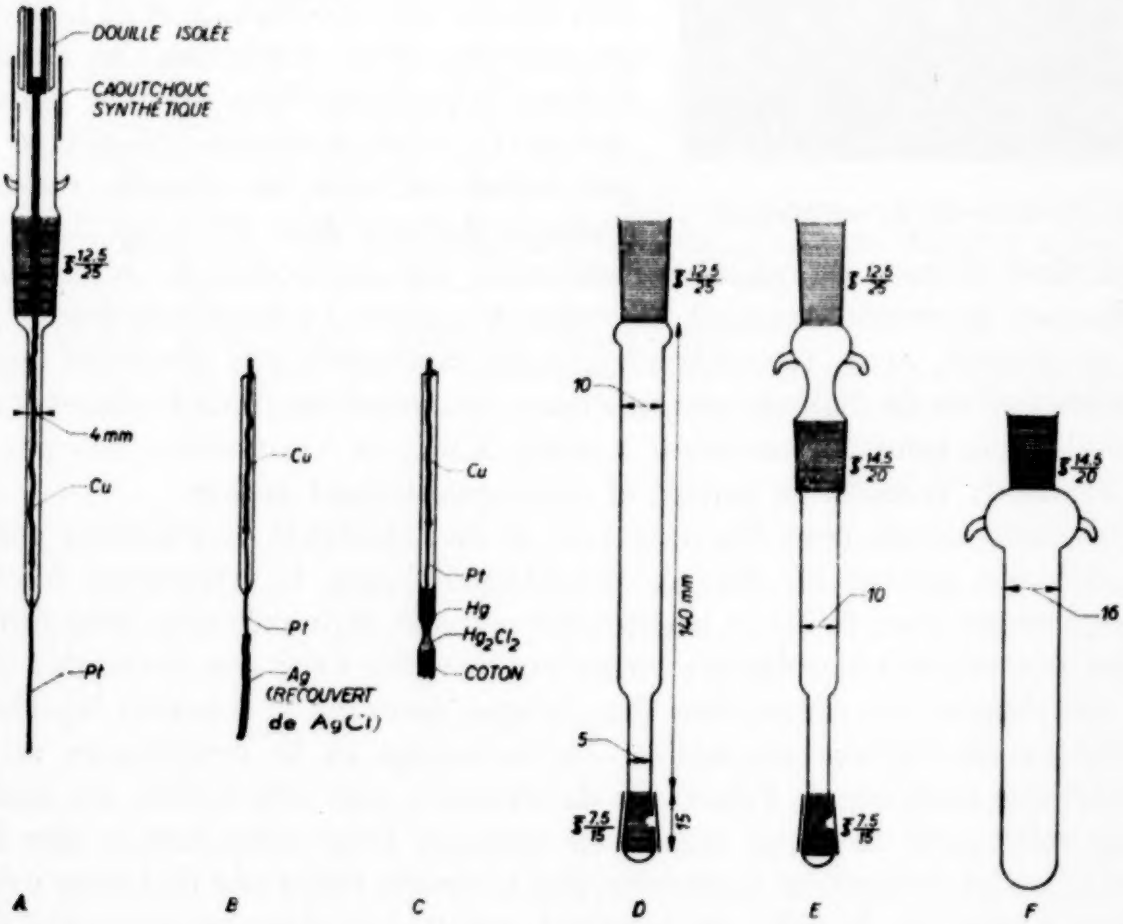

DOUILLE ISOLÉE
CAOUTCHOUC SYNTHÉTIQUE
$\mathfrak{F}\frac{12.5}{25}$
4 mm
Cu
Pt
Cu
Pt
Ag (RECOUVERT de AgCl)
Cu
Pt
Hg
Hg_2Cl_2
COTON
$\mathfrak{F}\frac{12.5}{25}$
10
140 mm
5
15
$\mathfrak{F}\frac{7.5}{15}$
$\mathfrak{F}\frac{12.5}{25}$
$\mathfrak{F}\frac{14.5}{20}$
10
$\mathfrak{F}\frac{7.5}{15}$
$\mathfrak{F}\frac{14.5}{20}$
16
A
B
C
D
E
F

Fig. 2. Electrode de référence

A: Electrode Pt
B: Electrode Ag/AgCl
C: Electrode au calomel
D: Tube plongeant simple
E: Tube plongeant
F: Tube protecteur pour E

Bibliographie p. 473.

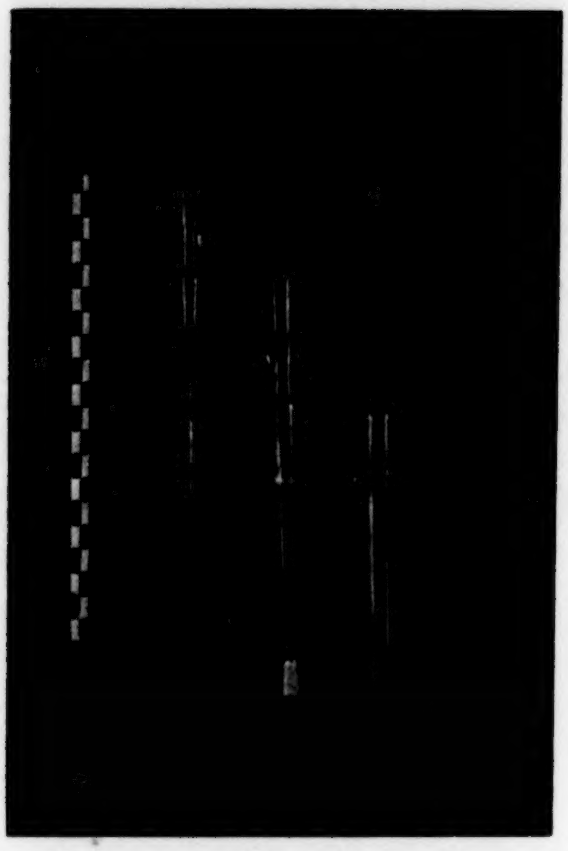


Fig. 3. Electrode de référence.

plonge directement dans la solution à analyser. Ces électrodes sont montées dans des tubes en verre fermés par un bouchon de gel d'agar-agar[6] ou de papier filtre[7], une plaque de verre fritté[8], un fil d'amiante soudé dans le verre[9], un tube capillaire[10] ou par un capuchon rodé[11]. Les électrodes de ce genre, et spécialement celle à fil d'amiante, sont utilisées de plus en plus. Les types connus et énumérés ci-dessus présentent cependant, à divers degrés, certains inconvénients (manque d'étanchéité, complexité de montage, difficulté de nettoyage et de remplissage, etc.). Pour les éviter, nous avons adopté la construction représentée par les Figs. 2 et 3. L'électrode proprement dite s'emboîte, à l'aide de rodages normalisés, dans le tube plongeant qui porte à son extrémité un rodage percé sur lequel s'adapte une douille rodée (ces rodages doivent être de grain fin). Cette construction permet de réaliser facilement les électrodes de références les plus diverses (électrode Ag/AgCl, électrode à potentiel d'inversion défini[12], électrode au calomel, etc.). Généralement, nous employons une électrode Ag/AgCl constituée par un fil d'argent partiellement recouvert de AgCl fondu et, comme électrolyte, une solution contenant 1 mol.g KNO_3 et 0.001 mol.g HCl par litre. Cette électrode possède un potentiel remarquablement stable.

La construction du pont électrolytique et de l'électrode de référence empêche toute diffusion gênant les dosages potentiométriques. La résistance électrique reste cependant assez faible et les mesures peuvent être exécutées sans difficulté avec un potentiomètre ordinaire lorsqu'on travaille avec des électrodes indicatrices métalliques. La disposition des rodages assurant la jonction liquide rend leur dislocation fortuite impossible. Le nettoyage et le remplissage du pont électrolytique ainsi que de l'électrode de référence sont très faciles. Un seul remplissage suffit pour un grand nombre de titrages. Pour renouveler le film d'électrolyte entre les rodages, on soulève un peu la douille rodée afin de laisser s'écouler quelques gouttes de liquide; on la remet ensuite en place en appuyant légèrement. (Il faut prendre garde qu'il n'y ait pas de bulle d'air dans l'orifice). Les rodages assurant la jonction liquide ne doivent pas être graissés. Pour éviter leur incrustation, on les maintient immergés dans de l'eau distillée lorsque le pont (ou l'électrode) n'est pas utilisé.

Le pont électrolytique et l'électrode de référence décrits ci-dessus sont utilisés depuis plus de deux ans dans nos laboratoires et ont donné entière satisfaction.

RÉSUMÉ

On décrit un pont électrolytique et une électrode de référence pour titrages potentiométriques.

SUMMARY

A salt bridge and a reference electrode for potentiometric titrations are described.

ZUSAMMENFASSUNG

Es werden ein Elektrolytschlüssel und eine Tauchelektrode für potentiometrische Titrationen beschrieben.

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A NEW METHOD FOR THE POTENTIOMETRIC DETERMINATION OF LEAD WITH ALKALINE PERMANGANATE

by

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The methods hitherto applied for the determination of lead depend mainly upon the precipitation of plumbous ions as an insoluble compound. In some of these cases as with the sulphide[1], sulphate[2] and ferrocyanide[3], the process could be followed potentiometrically. In this investigation a new method is devised, by the aid of which lead could be estimated with fair accuracy, depending upon its oxidation from the bivalent to the quadrivalent state with potassium permanganate in alkaline media. Advantage is taken of the amphoteric properties of lead hydroxide, which can readily dissolve in excess sodium hydroxide, after being primarily precipitated, yielding sodium plumbite. This latter product, when treated with oxidising agents such as sodium hypochlorite or potassium permanganate, yields different oxidation products, *viz.* Pb_3O_4 or Pb_2O_3 or PbO_2, depending on the conditions of the reaction. Potassium permanganate was preferred to other oxidants on account of its wider applicability in volumetric analysis, the ease of preparation and standardisation of its solutions and the considerable stability of the latter when well preserved.

The oxidation of sodium plumbite was performed both in weak and strong alkaline solutions permitting the reduction of permanganate to manganese dioxide and manganate, respectively[4]. Considering, now, that oxidation of bivalent lead proceeds completely to the quadrivalent state, the reactions taking place can be represented by the following equations:

a) in weak alkaline solutions,

$$2\ Mn^{+7} + 3\ Pb^{+2} \longrightarrow 3\ Pb^{+4} + 2\ Mn^{+4} \quad \ldots\ldots\ldots \quad (1)$$

b) in strong alkaline solutions,

$$2\ Mn^{+7} + Pb^{+2} \longrightarrow Pb^{+4} + 2\ Mn^{+6} \quad \ldots\ldots\ldots \quad (2)$$

The equilibrium constants of these two reactions, as calculated from the redox potentials of the systems PbO/PbO_2, MnO_4^-/MnO_2^- and MnO_4^-/MnO_4^{-2} which are equal to 0.250, 0.570 and 0.540 volt respectively, amount to $5.53 \cdot 10^{-33}$ and $1.55 \cdot 10^{-10}$ in weak and strong alkaline media. The corresponding values for the degree of completion amount to $3.09 \cdot 10^{-7}$ and $5.37 \cdot 10^{-4}$ respectively, indicating that both reactions can take place quantitatively.

EXPERIMENTAL

The titration device

The titration vessel is similar in its essential details to that previously described[6]. The indicator electrode consists of a platinum wire $\sim$ 1.5 mm in diameter. This latter was always abraded with emery paper, etched with aqua regia and rinsed several times with water before each experiment.

Preparation and standardisation of solutions

a) Potassium permanganate solutions were prepared as recommended by STAMM[7]. They were stored in brown-coloured glass bottles and standardised with sodium oxalate of grade AnalaR[8]. Now and then these solutions were checked for their oxidising power, which was found to be practically constant.

b) Bivalent lead solutions were prepared by dissolving an appropriate weight of PbO of grade AnalaR in the least amount of AnalaR nitric acid, and diluting the lead nitrate produced to the requisite volume with twice distilled water. The lead content of such solutions was estimated gravimetrically by precipitation as lead chromate. The average of eight determinations that yielded from 0.3138 — 0.3142 g $PbCrO_4$ per 25 ml of solution was used in calculating the concentration of lead, which amounted to 0.0778N. Another solution prepared and analysed as above was 0.1003N.

Working procedure

In the oxidation of sodium plumbite with potassium permanganate, 10 ml of the lead solution were delivered into the titration vessel and 5N NaOH solution added till complete dissolution of the precipitated lead hydroxide. More alkali and water were then added to bring the alkali concentration to that desired, and the total volume to 50 ml.

In the reverse process of titration, *i.e.* the reduction of potassium permanganate with the bivalent lead solution, the appropriate volume of the former was delivered into the titration vessel and mixed with 5N NaOH to bring about the desired alkalinity. Occasionally 5% $Ba(NO_3)_2$ solution was added in an amount sufficient to precipitate all the manganate ions formed by the reduction of permanganate.

RESULTS

Oxidation of plumbite with potassium permanganate

This reaction was found to be rather slow, needing for the attainment of equilibrium $\sim$ 15 min at the beginning of the titration and $\sim$ 30 min near the end-point. It could, however, be accelerated with sodium chloride, the concentration of which under optimum conditions amounts to 5%. Under these conditions the time for equilibrium was reduced to $\sim$ 3 min at the beginning and $\sim$ 10 min at the end of the reaction. By using other catalysts such as zinc or mercuric oxide the time needed for equilibrium was ∿ 3—5 min at the beginning of the titration and ∿ 2—3 min at the end-point.

The serious difficulty with this reaction, however, is that the indicator electrodes became probably poisoned during the reaction and unless strongly abraded with emery paper and etched with a fresh solution of aqua regia, no inflection could be observed at the end-point. In order to detect the position of the end-point clearly it is therefore advisable to use an electrode which has not been previously used in a similar titration. The maximum inflection in the titration curves, two of which are represented in Fig. 1, amounted to ∿ 50 mv per 0.1 ml of potassium permanganate. This value was only attained when the plumbite solution was diluted to 50 ml and became poorer as the concentration of lead increased. Using a tantalum rod instead of the platinum wire, a smaller inflection was observed amounting to ∿ 26—34 mv. With a gold electrode the end-point was reached 2.6% earlier and the inflection at the end-point was very poor (∿ 12 mv). The difficulty arising from the smallness of the inflection could, however, be overcome by the use of a 10-meters bridge, in which case the potential change at the end-point is magnified 10 times.

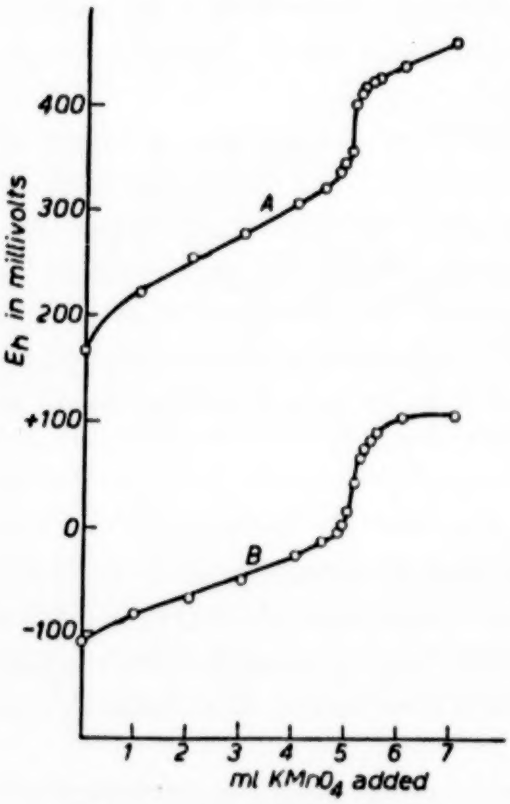

Fig. 1

Titration of 10 ml 0.1003 *N* Pb^{+2} solution with 0.06582 *N* $KMnO_4$.
(A) with platinum electrode,
(B) with tantalum electrode.

It is noteworthy to remark that after this inflection has occurred, the further addition of permanganate did not colour the solution pink, indicating that some reaction still took place. Since the amount of oxidant consumed till the maximum inflection is only $^1/_3$ of that needed for complete oxidation of PbO into PbO_2, even in the presence of ZnO or HgO[9], the product of oxidation of plumbite is most probably Pb_3O_4. The disappearance of the permanganate colour is possibly due to its consumption in the oxidation of Pb_3O_4 into higher oxides. This conclusion is confirmed by the appearance of a green colour resulting from the reduction of potassium permanganate to manganate.

Oxygen of the atmosphere has no apparent effect on the result, since the titration performed in an atmosphere of nitrogen did not differ appreciably from those carried out in aerated solutions.

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TABLE 1A

TITRATION OF Pb^{+2} SOLUTION WITH $KMnO_4$ USING NaCl AS CATALYST, AND DILUTING TO 50 ml, AT 30° C

	Max. inflection per 0.1 ml $KMnO_4$	mg Pb present	mg Pb found	error %
a) 10 ml 0.1003*N* Pb^{+2} titrated with 0.06582*N* $KMnO_4$:				
plumbite, no excess alkali	49	103.9158	103.5573	—0.35
,, in 0.1*N* NaOH	10	,,	103.5157	—0.39
,, ,, ,, ,,	47	,,	103.6196	—0.29
,, ,, ,, ,, (tantalum electrode)	26	,,	104.2224	+0.29
plumbite in 0.1*N* NaOH (gold electrode)	12	,,	101.1879	—2.63
plumbite, in 0.2*N* NaOH	34	,,	103.5677	—0.34
,, in 0.4*N* NaOH	16	,,	103.4118	—0.49
b) 0.1003*N* Pb^{+2}, as sodium plumbite, in 0.1*N* NaOH:				
20 ml titrated with 0.0629*N* $KMnO_4$	10	207.8316	208.2265	+0.19
5 ml titrated with 0.03145*N* $KMnO_4$	15	51.9579	52.2654	+0.38
10 ml (not diluted) titrated with 0.0821*N* $KMnO_4$	19	103.9158	104.5549	+0.61

TABLE 1B

TITRATION OF 10 ml 0.1003*N* Pb^{+2}, AS PLUMBITE, IN 0.1*N* NaOH WITH 0.0821*N* $KMnO_4$ AND DILUTING TO 50 ml, AT 30° C

	Max. inflection per 0.1 ml $KMnO_4$	mg Pb present	mg Pb found	error %
ZnO as catalyst	28	103.9158	103.1852	—0.73
HgO ,, ,,	23	,,	103.4066	—0.49

Reduction of potassium permanganate in this reaction proceeds probably to MnO_2 since the alkali concentration is usually kept as low as 0.1*N*. When the alkali concentration was increased to 1—2.5*N*, reduction of the permanganate yielded a mixture of manganate and manganese dioxide without the appearance of an inflection. The reaction taking place in the weaker alkaline solutions can, however, be represented by the equation:

$$9\ PbO + 2\ MnO_4^- + H_2O \longrightarrow 3\ Pb_3O_4 + 2\ MnO_2 + 2\ OH^-$$

in which 6 electrons are involved in the reduction of permanganate. Considering the redox potential of the system PbO/Pb_3O_4 to be 0.241 volt as calculated from free energy data[10], the equilibrium constant and the degree of completion for the above reaction amount to $3.9 \cdot 10^{-31}$ and $7.4 \cdot 10^{-11}$, respectively.

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Representative results obtained under a variety of conditions are shown in Tables IA and IB. These indicate that the errors in the concentration of lead as calculated on the basis of formation of Pb_3O_4 vary from —0.73 to + 0.61%.

Reduction of permanganate with bivalent lead

This reaction was performed in both weak and strong alkaline media. As may seen from the curves shown in Fig. 2, curve A, which represents a titration performed in either 0.1*N* or 0.5*N* NaOH, is not characterised by an inflection at the end-point. Reduction of potassium permanganate under these conditions apparently yields a mixture of manganate and manganese dioxide. At higher alkali concentration, *viz.* 1.5 — 3.5*N* NaOH, reduction of permanganate is more favoured to the manganate state. Curve B which represents a titration made under these latter conditions is characterised by an inflection which is on the whole sharper than in the oxidation of plumbite with permanganate, amounting to about 40 mv per 0.1 ml of Pb^{+2} solution.

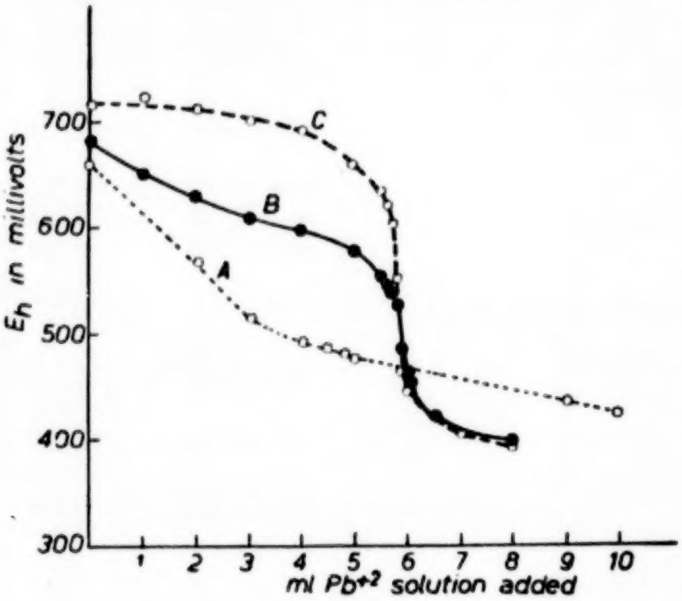

Fig. 2
Titration of 25 ml 0.0183*M* $KMnO_4$ with 0.0778*N* Pb^{+2} solution.
(A) in 0.1—0.5*N* NaOH, (B) in 2.5*N* NaOH, (C) in 1*N* NaOH + Ba^{+2} ions.

This reaction takes place rapidly at the beginning of the titration, but slows near the end-point needing ∿5 min for the attainment of the equillibrium. It can, however, be accelerated by using as a catalyst a mixture of ZnO and HgO, when under these conditions it needs 1 — 2 min for equilibrium. ZnO alone is a better catalyst than HgO but the mixture of the two oxides is better than either of them. The use of this catalyst has as its main object the oxidation of PbO to PbO_2[9], but the same result was obtained in the absence of both oxides.

By varying the alkali concentration from 1.5 — 3.5*N*, it was established that at ∿2.5*N* NaOH the reaction takes place more or less quantitatively in the presence of the mixture catalyst. The errors in this case as may be seen from the results shown in Table II, vary from + 0.17 to — 0.26%. At higher alkali concentration than 2.5*N* NaOH the errors increase due probably to the autodecomposition of permanganate[4], and at lower alkali due to its partial reduction to MnO_2.

In these titrations in which lead nitrate solutions were used as titrant, the volume consumed up to the end-point was found to depend largely on the rate of its addition. When the titrant was added one ml at a time the errors became considerable amounting to ∼ 7.38% (*cf.* Table IV). If on the other hand each addition was made dropwise, the errors reduced to ∼ 0.20%. It is advisable in performing this titration to add the lead solution dropwise while vigorously stirring the permanganate. This serves to prevent local concentration of bivalent lead which, perhaps, might lead to partial reduction of the MnO_4^- ions to MnO_2

TABLE II

TITRATION OF $KMnO_4$ WITH Pb^{+2} SOLUTION, USING $HgO + ZnO$ AS CATALYST, AT 30° C

	Max. inflection per 0.1 ml of Pb^{+2} solution	mg Pb equivalent to $KMnO_4$	mg Pb in the lead solution consumed	error %
a) 25 ml 0.0183*M* $KMnO_4$ titrated with 0.0778*N* Pb^{+2} solution:				
in 2*N* NaOH	28	47.3957	47.8794	+1.02
,, 2.5 ,, ,, (no catalyst)	24	,,	47.5570	+0.34
,, 2.5 ,, ,,	40	,,	47.4763	+0.17
,, ,, ,, ,,	28	,,	47.2748	−0.26
,, 3.5 ,, ,,	43	,,	46.7511	−1.36
b) 25 ml 0.02446*M* $KMnO_4$ with 0.1003*N* Pb^{+2}:				
in 1.5*N* NaOH	45	63.3888	65.5710	+3.44
,, 2.5 ,, ,, (at 60° C)	55	,,	57.8812	−8.69

In order to overcome the difficulty arising from the dependence of the results on the rate of adding the titrant, the trial was made to capture the manganate ions as soon as they form by precipitation as $BaMnO_4$, using for this purpose the requisite amount of a 5% solution of $Ba(NO_3)_2$. Addition of double the equivalent amount of Ba^{+2} ions has no serious effect on the result. Ba^{+2} ions were not, however, effective in capturing the manganate ions unless the alkalinity was sufficient for the reduction to take place to the manganate state. Thus, as may be seen from the results shown in Table III, the errors amount to 5.74% in the presence of 0.5*N* NaOH and become less pronounced when the alkali concentration is made 1 — 1.5*N*. The alkali concentration suitable for the reaction to take place with the least error should, therefore, not be higher than 1.5*N* at the beginning of the titration and not lower than 0.75*N* at the end-point. At alkali concentrations lower than 0.75*N*, the errors increase due to the partial reduction of permanganate to MnO_2. The same occurs also at alkali concentrations higher than 1.5*N* due to the autodecomposition of MnO_4^- ions, a process which is probably catalysed by the precipitation of $BaMnO_4$.

Another advantage of the use of Ba^{+2} ions is that the inflections at the end-points, as may be seen from curve C in Fig. 2, are however sharper than in the absence of these ions amounting to $\sim$ 0.1 volt per 0.1 ml of the lead solution and the curves smoother.

The errors due to the autodecomposition of $KMnO_4$ at alkalinities higher than 1.5N NaOH in the presence of Ba^{+2} ions and than 2.5N NaOH in the absence of these ions could be overcome by performing blank experiments, as may be seen from the results shown in Table IV.

Both in the presence and in the absence of Ba^{+2} ions, heat favours the autodecomposition of the MnO_4^- ions, leading to considerable errors which are higher in the former than in the latter case.

TABLE III

TITRATION OF $KMnO_4$ WITH Pb^{+2} SOLUTION IN PRESENCE OF Ba^{+2} IONS, USING $HgO + ZnO$ AS CATALYST, AT 30° C

	Max. inflection per 0.1 ml of Pb^{+2} solution	mg Pb equivalent to $KMnO_4$	mg Pb in the lead solution consumed	error %
a) 25 ml 0.02446M $KMnO_4$ titrated with 0.1003N Pb^{+2}:				
in 0.5N NaOH	78	63.3888	67.0258	+5.74
,, 1 ,, ,,	87	,,	63.5966	+0.32
,, 1.5 ,, ,,	70	,,	63.1809	—0.32
,, 2 ,, ,,	90	,,	61.1026	—3.74
,, 2.5 ,, ,,	91	,,	59.5439	—6.07
,, 1 ,, ,, (60° C)	94	,,	53.6207	—15.24
0.0274M $KMnO_4$ in 0.75N NaOH	80	72.0138	72.5334	+0.72
b) 25 ml 0.0183M $KMnO_4$ titrated with 0.0788N Pb^{+2}:				
in 0.5N NaOH	81	47.3957	51.1842	— 7.99
,, 0.85N ,, ,,	87	,,	47.2748	— 0.26
,, 1 ,, ,,	89	,,	47.2345	— 0.34
20 ml $KMnO_4$ in 1N NaOH (no catalyst)	145	37.9650	38.1262	+0.42

TABLE IV

TITRATION OF 20 ml 0.02096M $KMnO_4$ WITH 0.1003N Pb^{+2}, USING $HgO + ZnO$ AS CATALYST, AT 30° C

	mg Pb equivalent to $KMnO_4$	mg Pb in solution	error %	error from blank	exp. error %
in 2N NaOH + Ba^{+2} ions	43.4310	42.3003	—2.58	—2.25	—0.33
,, ,, ,, ,, ,, ,,	43.4310	42.1889	—2.86	—2.45	—0.41
,, 3.5N NaOH	43.4310	41.8805	—3.57	—3.30	—0.27

By decreasing the concentration of both $KMnO_4$ and Pb^{+2} solutions, it was possible to obtain good results when $KMnO_4$ is made 0.0026*M* and the lead 0.0301*N*. At still lower concentration for both reactants, large errors were observed as may be seen from the results shown in Table IV.

It is noteworthy to remark that although the errors due to the rapid addition of the lead solution decreased more in the presence of Ba^{+2} ions than in their absence, yet they still manifested themselves considerably. Thus by adding the lead solution 1 ml at a time, the errors amounted to ∼ 3.77% as compared with ∼ 7.38 in the absence of Ba^{+2} ions. Good results could only be obtained as in the latter case, when the lead solution is added dropwise while continually stirring the permanganate solution.

The trial was further made to overcome the dependence of the result on the rate of addition, by using instead of the 0.1003*N* lead nitrate solution, a twice diluted sodium plumbite as titrant. Sodium plumbite, prepared by just dissolving the lead hydroxide, leads also when added 1 ml at a time, as may be seen from the results shown in Table V, to some error which, although smaller than in the case of the lead nitrate solution, is still pronounced amounting to 1.9%. When, on the other hand, the plumbite solution was made 1 or 2.5*N* with respect to

TABLE V

TITRATION OF $KMnO_4$ WITH Pb^{+2} SOLUTION IN THE PRESENCE OF 1*N* NaOH, Ba^{+2} IONS AND ZnO+HgO AS CATALYST, AT 30° C

	Max. inflection per 0.1 ml Pb^{+2} solution	mg Pb equivalent to $KMnO_4$	mg Pb in the lead solution consumed	error %
a) Using 0.05015*N* Pb^{+2} solution:				
25 ml 0.02446*M* $KMnO_4$	48	63.3888	63.1287	—0.41
15 ml ,, ,, ,,	83	38.0333	38.1891	+0.41
5 ml ,, ,, ,,	132	12.6778	12.7297	+0.41
25 ml 0.01223 ,, ,,	61	31.6944	31.8243	+0.41
b) Using 0.0301*N* Pb^{+2}:				
10 ml 0.02446*M* $KMnO_4$	71	25.3555	25.4492	+0.37
12.5 ml ,, ,, ,,	35	31.6944	31.7863	—0.29
50 ml 0.004892*M* $KMnO_4$	80	25.3555	25.3251	—0.12
50 ml 0.002446*M* $KMnO_4$	133	12.6778	12.6458	—0.25
10 ml 0.02446*M* $KMnO_4$ (0.7*N* alkali)	47	25.3555	25.6978	+1.35
c) Using 0.01*N* Pb^{+2}:				
5 ml 0.02446*M* $KMnO_4$	46	12.6778	11.9197	—5.98
25 ml 0.004892*M* $KMnO_4$	56	12.6778	12.0122	—5.25
25 ml 0.002446 ,, ,,	107	6.3389	5.7672	—9.02

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NaOH, according to whether Ba^{+2} ions were present or not, results were found to be less dependent on the rate of addition. One can therefore conclude that the errors due to the rapid addition of the lead solution not made alkaline with NaOH could be attributed both to the local concentration of the bivalent lead and to the local improverishment of the OH^- ion concentration in the region where the titrant first mixes with the permanganate solution, leading to its partial reduction to MnO_2 and accordingly to the considerable errors observed. Care must, then, be taken in performing these titration that the lead solution, preferably in the form of sodium plumbite, mixed with the appropriate amount of alkali, should be in the region of 0.05N, and not too rapidly added.

TABLE VI

TITRATION OF $KMnO_4$ WITH BIVALENT LEAD SOLUTION, RAPIDLY ADDED

	Max. inflection per 0.1 ml Pb^{+2}	mg Pb equivalent to $KMnO_4$	mg Pb in the lead solution consumed	error %
a) 0.02446M $KMnO_4$ with 0.1003N Pb^{+2}:				
25 ml $KMnO_4$ in 2.5N NaOH	47	63.3888	68.0650	+7.38
,, ,, ,, ,, 1 ,, ,, , + Ba^{+2} ions	64	,,	65.7788	+3.77
b) 0.02096M $KMnO_4$ with 0.05015N sodium plumbite:				
20 ml $KMnO_4$ in 2.5N NaOH	45	43.4310	45.3680	+4.46
,, ,, ,, ,, 1 ,, ,, + Ba^{+2} ions	80	,,	44.2562	+1.90
25 ml $KMnO_4$ with plumbite both 2.5N in alkali				
rapid	43	54.2888	54.1314	—0.29
dropwise	49	,,	54.1921	—0.18
12.5 ml $KMnO_4$ with plumbite, both 1N NaOH + Ba^{+2} ions				
rapid	83	27.1444	27.2339	+0.33
dropwise	80	,,	27.2123	+0.11

Determination of different quantities of lead

It was further tried to determine the amount of lead present in a given solution by adding the latter, preferably in the form of sodium plumbite which was made 1N with respect to sodium hydroxide, dropwise and with vigorous stirring to an excess of potassium permanganate mixed with the requisite amount of Ba^{+2} ions together with the appropriate quantity of NaOH to bring the alkalinity to 1N.

Trial to determine the excess of permanganate with a standard solution of ferrous iron or oxalic acid in acid medium failed owing to the interference of

PbO_2 originally formed through the oxidation of bivalent lead as may be seen from the following experiment:

3 ml of lead solution containing 31.1748 mg Pb were added dropwise with constant stirring to 25 ml of 0.0183*M* $KMnO_4$ mixed with 25 ml of 5*N* NaOH without the addition of Ba^{+2} ions. This solution was quantitatively poured onto 50 ml of ∼ 5.5*N* H_2SO_4. 35 ml of 0.0907*N* ferrous ammonium sulphate were then added. The excess of the ferrous iron was back-titrated with 0.0183*M* $KMnO_4$, when it needed 4.03 ml, so that the total volume of the oxidant consumed in the whole process amounted thus to 29.03 ml.

Since 35 ml of the ferrous ammonium sulphate solution are equivalent to 29.05 ml of 0.0183*M* $KMnO_4$ it could be concluded that lead dioxide initially formed was reduced again by the ferrous solution.

Similar conclusion could be drawn if oxalic acid is used instead of ferrous iron, as this compound is also readily oxidised with PbO_2 in hot acid solution[11].

Recourse was therefore taken to determine the excess $KMnO_4$ potentiometrically with a standard lead or plumbite solution following the above procedure, in the presence of Ba^{+2} ions and a mixture of ZnO and HgO as catalyst. The alkali concentration should not, as stated above, be higher than 1.5*N* at the beginning and not lower than 0.75*N* after titrating the excess permanganate with the bivalent lead solution. Table VII contains some representative results, which indicate that amounts of lead as low as 31 mg could be estimated by this methods with fair accuracy.

TABLE VII

Volume and molarity of $KMnO_4$ solution	mg Pb equivalent to total $KMnO_4$	mg Pb equivalent to excess $KMnO_4$	mg Pb to be determined	mg Pb found	error %
25 ml 0.02446*M* $KMnO_4$	63.3888	32.3178	31.1748	31.0710	—0.33
50 ml ,, ,, ,,	126.7776	23.3255	103.9158	103.5521	—0.35
50 ml 0.02194*M* ,,	113.6839	72.3255	41.5664	41.3584	—0.48
50 ml ,, ,, ,,	113.6839	41.1680	72.7412	72.6159	—0.17

SUMMARY

A new method for the estimation of lead, based on its oxidation from the bivalent to the quadrivalent state by alkaline permanganate has been devised. The reaction takes place so rapidly in the presence of a mixture of ZnO and HgO that it can be followed potentiometrically. Oxidation of sodium plumbite with $KMnO_4$ leads to the formation of Pb_3O_4 and MnO_2. Reduction of $KMnO_4$ with Pb^{+2} ions or with sodium plumbite proceeds almost quantitatively in 2.5*N* NaOH in the absence of Ba^{+2} ions and in 1—1.5*N* NaOH in the presence of these ions. Under these conditions $Pb^{+2} \rightarrow Pb^{+4}$ and $MnO_4^- \rightarrow MnO_4^{-2}$, provided that the lead solution is not added too rapidly.

RÉSUMÉ

Une nouvelle méthode a été mise au point pour le dosage du plomb; elle est basée sur son oxydation de l'état bivalent à l'état tétravalent, à l'aide de permanganate alcalin. En présence d'un mélange de ZnO et de HgO, la réaction a lieu si rapidement qu'elle peut être suivie potentiométriquement. L'oxydation du plombite de sodium par $KMnO_4$ conduit à la formation de Pb_3O_4 et MnO_2. La réduction de $KMnO_4$ par l'ion Pb^{+2} ou par le plombite de sodium a lieu presque quantitativement en solution de NaOH 2.5N en l'absence d'ions Ba^{+2}, et en solution de NaOH 1—1.5 en présence d'ions Ba^{+2}. Dans ces conditions: $Pb^{+2} \rightarrow Pb^{+4}$ et $MnO_4^- \rightarrow MnO_4^{-2}$, à condition que la solution de plomb ne soit pas ajoutée trop rapidement.

ZUSAMMENFASSUNG

Es wurde eine neue Methode für die Bestimmung von Blei, welche auf der Oxydation von zwei-wertigem zu vier-wertigem Blei mit alkalischer Permanganatlösung beruht, ausgearbeitet. In einer Mischung von ZnO und HgO geht die Reaktion so rasch vonstatten, dass sie potentiometrisch verfolgt werden kann.

Die Oxydation von Natriumplumbit mit $KMnO_4$ führt zur Bildung von Pb_3O_4 und MnO_2. Die Reduktion von $KMnO_4$ mit Pb^{+2}-Ionen oder Natriumplumbit findet quantitativ in 2.5N NaOH in Abwesenheit von Ba^{+2}-Ionen und mit 1—1.5N NaOH in deren Anwesenheit statt. Unter diesen Bedingungen ergibt $Pb^{+2} \rightarrow Pb^{+4}$ und $MnO_4^- \rightarrow MnO_4^{-2}$. Die Bleilösung darf nicht zu schnell zugesetzt werden.

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THE AMPEROMETRIC DETERMINATION OF ZINC WITH POTASSIUM FERROCYANIDE

USE OF ROTATING PLATINUM ANODE

by

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The titration of zinc ions with potassium ferrocyanide, which has been a standard method of zinc analysis for many years, depends on the formation of the insoluble potassium zinc ferrocyanide $K_2Zn_3[Fe(CN)_6]_2$[3].

Titrations have been carried out potentiometrically, or by the use of either internal or external indicators, using empirical conditions of temperature, acid, volume, amount of ammonium chloride present, and the rate of titration. More recently, methods have been described utilizing an amperometric end-point with a rotating platinum electrode[1], with a dropping mercury electrode[6], and a dead-stop end-point[5]. CHOVNYK AND KUZ'MINA[2] reported on an amperometric study of the reaction of precipitation of nickel, zinc, and copper ferricyanides.

This investigation was undertaken to develop a rapid, accurate titration method for determination of zinc in ores, flue dusts, and other metallurgical products. Because the basic reaction is identical with that previously used for the classical titration methods, no study of interferences was made. However, there is no reason to believe that the interferences would be any different than those described by HILLEBRAND AND LUNDELL[3] and their scheme for sample preparation can be employed prior to the application of the amperometric titration.

APPARATUS AND REAGENTS

The apparatus for the amperometric titration consists of a rotating platinum electrode and a Fisher Elecdropode (Fisher Scientific Co., Pittsburgh, Pa.). The Elecdropode is used to apply a 1 volt difference in potential between a saturated calomel electrode and the platinum anode and to measure the anodic current produced.

Lipless beakers of various sizes are used as titration vessels. A small hotplate is used to heat the solution before titration and to serve as a stand for the vessel.

A standard solution of zinc ion was prepared by weighing exactly 4.0690 g of reagent grade zinc oxide (Mallinckrodt) and dissolving it in a slight excess of hydrochloric acid. Upon dilution to 1 liter with distilled water, this solution is $0.05M$ as used in the titration:

$$3\ ZnCl_2 + 2\ K_4[Fe(CN)_6] \longrightarrow K_2Zn_3[Fe(CN)_6]_2 + 6\ KCl$$

A potassium ferrocyanide solution is obtained by dissolving 14.1 g of C.P. potassium ferrocyanide trihydrate in 1 liter of distilled water. This solution, which is approximately $0.033M$, is standardized against known aliquots of the standard zinc solution by the amperometric titration procedure given below.

PROCEDURE

Solids. Weigh a suitable size sample into a 300-ml Erlenmeyer flask and add 0.1 g of ferric sulfate to aid in removing impurities such as arsenic, antimony, tellurium, and selenium. If the material contains between 10 and 50% zinc, use a 0.5-g sample. If the material contains less than 10% zinc, use 0.5 to 2.0 g of sample. Wet the sample with distilled water and add 10 ml of concentrated hydrochloric acid, 15-25 ml of $18N$ sulfuric acid, and 10 ml of concentrated nitric acid. Heat the mixture until strong fumes of sulfuric acid are evolved. Cool and add 40 ml of distilled water. Heat to 80° C and add 5 g of ammonium chloride, 0.25 g of ammonium persulfate, and 25 ml of concentrated ammonium hydroxide. Boil the solution for 5-6 minutes. Remove and filter rapidly through No. 1 Whatman paper. Wash the flask and filter paper with hot ammonium chloride wash solution (50 g of ammonium chloride and 50 ml of ammonium hydroxide in 1 liter of distilled water). Add a few drops of methyl orange to the filtrate and make just acid with hydrochloric acid. Then add 3 ml in excess. Add 10 g of test lead and boil for 10 minutes. Decant the liquid from the test lead into a 400-ml beaker and wash the lead with several small portions of water. Dilute the solution to approximately 250 ml with distilled water. Place the solution on a hot plate and insert the electrodes into the solution. Impress a potential of $+1.0$ volts on the rotating platinum electrode and maintain the temperature of the solution at 65° C ± 10° C. Add standard potassium ferrocyanide solution from a burette in small increments, allowing the galvanometer reading to become steady after each addition. Record the volume of reagent added and the galvanometer reading. Continue in this manner until the bend in the titration curve is passed and take a few more readings after this point. (The readings at the beginning are very low and remain thus until an excess of ferrocyanide ion has been added. Toward the end-point, the current readings increase in proportion to reagent addition.)

Plot the volume of ferrocyanide added against the current readings obtained and draw straight lines through the two intersecting series of points. From the end-point thus obtained, calculate the amount of zinc in the sample.

Solutions. By any suitable procedure obtain an aqueous solution free from interfering substances and add ammonium hydroxide, hydrochloric acid, and water in accordance with the data given in Table I below. Heat the solution to 65° C ± 10° C and titrate with ferrocyanide solution of the appropriate strength.

TABLE I

CONDITIONS FOR AMPEROMETRIC TITRATION OF ZINC

Expected concentration Zinc (milliequivalents)	0.20 — 1.0 m.e. Zn	0.1 — 0.20 m.e. Zn	0.05 — 0.1 m.e. Zn
ml conc. NH_4OH	15	10	5
ml excess $12N$ HCl	3	2	1
final volume	250	50	36
conc. of $K_4[Fe(CN)_6]$	$0.0333M$	$0.0033M$	$0.0033M$
sensitivity	20 ×	20 ×	10 ×

If less than 0.02 milliequivalents of zinc is found, the titration will not be satisfactory. The determination should be repeated adding 5 ml of standard $0.01N$ zinc solution (standardized by titration under identical conditions) before adjusting the initial volume of the solution. From the total titration at the end-point, subtract the titration corresponding to the added zinc solution.

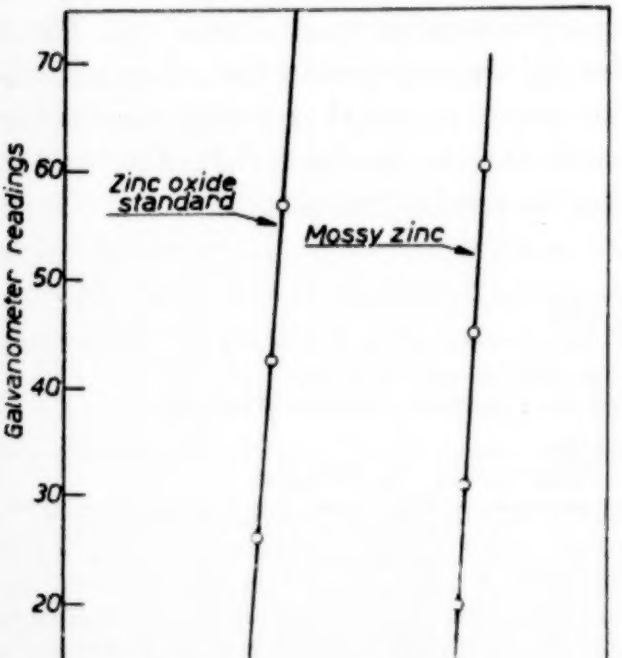

Fig. 1. Titration of zinc solutions with standard ferrocyanide solution.

References p. 490.

EXPERIMENTAL

The oxidation of ferrocyanide ion at a rotating platinum anode is very similar to the oxidation of ferrous ion reported by KOLTHOFF AND MAY[4]. Typical curves for the titration of solutions containing 0.3000 g of zinc oxide and 0.2500 g of zinc metal with $0.05M$ potassium ferrocyanide solution are shown in Fig. 1. It will be noted that there is virtually no slope before the end-point and that the oxidation of ferrocyanide ion after the end-point produces a series of points in a straight line. The reaction for the precipitation of zinc does not lend itself to a micro determination and the best results were obtained when relatively large samples of zinc were analyzed. In a series of titrations, various known amounts of zinc ion were titrated with potassium ferrocyanide solution at a temperature of 65° C ± 10° C, using the conditions described in the procedure above. The results obtained demonstrate that satisfactory analyses can be obtained when more than a few milligrams of zinc are present.

TABLE II

AMPEROMETRIC TITRATION OF ZINC WITH POTASSIUM FERROCYANIDE

Zinc added, mg	Zinc found, mg	Ferrocyanide, Molarity
1.60	1.59	0.0033
1.60	1.60	0.0033
3.30	3.38	0.0033
3.30	3.20	0.0033
6.50	6.56	0.0050
16.0	16.0	0.0333
16.0	15.7	0.0333
160	157	0.067
160	156	0.067

This method has been applied to the analysis of a variety of materials containing zinc, including flue dusts, high purity zinc oxide, ores, and zinc alloys. A typical group of analyses on purified zinc oxide materials is given in Table III. These analyses were carried out using the procedure given above for solids. The normality of the potassium ferrocyanide was approximately 0.0333M and was standardized by titration against a standard zinc solution made from C.P. zinc metal. Included in the table are duplicate of reagent grade zinc oxide.

TABLE III

ANALYSIS OF PURIFIED ZINC OXIDE MATERIALS
BY AMPEROMETIC TITRATION WITH POTASSIUM FERROCYANIDE

Sample No.	Zinc oxide, % Weight
1	98.9
	99.0
2	98.2
	99.0
3	99.4
	99.7
4	98.9
	98.7
5	99.2
	99.7
6*	99.9
	100.1

* Reagent grade zinc oxide.

References p. 490.

Two reagent grade chemicals, C.P. Mossy Zinc (Baker's) and zinc sulfate heptahydrate (Mallinckrodt's) were analyzed in triplicate using this method. The data, together with theoretical zinc content of the zinc sulfate, are given in Table IV.

TABLE IV

ANALYSIS OF REAGENT GRADE CHEMICALS FOR ZINC BY AMPEROMETRIC TITRATION WITH POTASSIUM FERROCYANIDE

Sample	Zinc content, % Weight
1. Baker's C.P. mossy zinc	100.12
max. impurities — 0.0081%	100.12
	100.18
2. $ZnSO_4 \cdot 7\ H_2O$ Mallinckrodt's	22.79
Theoretical Zn content = 22.74%	22.79
	22.81

DISCUSSION

The amperometric titration of zinc with potassium ferrocyanide at a rotating platinum electrode has several advantages over previously used methods. The end-point detection is very simple, eliminating the disadvantages of an external indicator such as uranyl nitrate. The titration is rapid, requiring less than 5 minutes for completion after the preparation of the solution. The method is suitable for application to a variety of zinc-containing materials, including those of high zinc content, and gives satisfactory reproducibility and accuracy on materials such as purified zinc oxide, slab zinc, and zinc-base die-casting alloy.

SUMMARY

A procedure is described for the determination of zinc by amperometric titration with potassium ferrocyanide. The reaction is carried out in a solution heated to approximately 65° C to obtain reproducible results. The method is suitable for application to a variety of zinc-containing materials including those of high zinc content. It gives satisfactory results on materials such as purified zinc oxide, slab zinc, ores, and flue dusts.

RÉSUMÉ

Une méthode est décrite pour la détermination du zinc par titration ampérométrique avec le ferrocyanure de potassium. La réaction est effectuée à environ 65° C pour obtenir des résultats reproductibles. Cette méthode convient pour le dosage du zinc dans un grand nombre de composés, même lorsque la teneur en zinc est élevée. On obtient de bons résultats avec des substances telles que: oxyde de zinc purifié, lingots de zinc, minerais et poussières de tuyaux.

References p. 490.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Bestimmung von Zink durch amperometrische Titration mit Ferrocyankalium beschrieben.

Um reproduzierbare Werte zu erhalten wird die Reaktion in einer auf ungefähr 65° C erwärmten Lösung ausgeführt. Das Verfahren ist auf viele Zink-enthaltende Stoffen auch bei hohem Zu-Gehalt anwendbar. Es gibt befriedigende Werte bei verschiedenen Materialen, wie Zinkweiss, Zinkmetallplatten, Erzen und Flugstäuben zu erreichen.

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BEGRIFFSKLÄRUNG IN DER pH-LEHRE*

von

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Gegenüber der zugegebenen Tatsache, dass es in wässrigen Lösungen nur H_3O^+-Ionen gibt, wiederholt EECKHOUT[2] (S.198) den klassischen Einwand: „Equilibrium equations, however, are not changed, and it is general practice to write H^+ instead of $(H_3O)^+$". Damit lässt sich kaum meine Ansicht widerlegen, dies sei „a custom more honoured in the breach than the observance" und *h* sei das einfachste und empfehlenswerteste Symbol für die Hydronium-Konzentration.

Immerhin, das ist Ansichtssache. Kaum bestreitbar scheint dagegen, dass man heutzutage *starke* Elektrolyte nicht ohne Einführung von Aktivitätskoefficienten behandeln darf. Wollte EECKHOUT dem entgegenhalten, dass die Schwefelsäure in ihrer zweiten Stufe doch keine wirklich starke Säure mehr sei, sondern nur mittelstark („fairly strong"), so wäre ihm zu erwidern, dass er sich in einem perfekten circulus vitiosus bewegt: Zu dieser Annahme kommt man nur, wenn man erst die Theorie der starken Elektrolyte vernachlässigt, mit Hilfe dieser unzulässigen Vernachlässigung folgert, dass die Schwefelsäure nicht stark sei, und daraufhin die Vernachlässigung als zulässig erklärt.

Numerisch kommt dabei folgendes heraus: EECKHOUT errechnet zunächst für $NaHSO_4$ 0.01*M* einen „anormalen" Wert: pH = 1.85, also $h = 1.4 \cdot 10^{-2}$. Dieser Wert ist nicht anormal sondern unmöglich, denn mehr als $1 \cdot 10^{-2}$ val/l an abdissoziierbarem H ist überhaupt nicht vorhanden. Dann einen „genaueren" Wert: pH = 2.14, also $h = 0.69 \cdot 10^{-2}$. Dieser Wert ist falsch, denn die Hydronium-*Konzentration* (EECKHOUT wiederholt, dass er nicht etwa Aktivität gemeint hat) ist 10^{-2}, nicht mehr und nicht weniger. Und für Na_2SO_4 in 0.1*M*-Lösung errechnet er pH = 7.35, also $h = 0.45 \cdot 10^{-7}$ und $oh = 2.2 \cdot 10^{-7}$, so dass Natriumsulfat alkalisch reagieren müsste. Es ist aber neutral. Auf die EECKHOUTsche Messung, die das Gegenteil beweisen soll, gehe ich später ein.

Diesen ganzen Rechnungen liegt eine offenbar Tabellen-Werken entnommene zweite Dissoziationskonstante der Schwefelsäure vom Zahlenwert $10^{-1.7}$ zu grunde[4]

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* Schlusswort an J. EECKHOUT[1,2].

Literatur S. 493.

(andere Tabellen[5] geben $10^{-1.92}$); an gleicher Stelle[4] findet man für $0.5N$ Lösungen bei 25° C folgende Dissoziationsgrade: HCl: 0.878; HBr: 0.899; HI: 0.901; $HMnO_4$: 0.933. Niemand wird daraus folgern, dass die Stärke der Säuren in dieser Reihenfolge zunimmt, sondern dass die Aktivitätskoeffizienten durch Cl^- stärker abgesenkt werden als durch Br^-, durch Br^- stärker als durch I^-, und durch I^- stärker als durch MnO_4^-. Die Tabelle hat das Wort „scheinbar" vor: Dissoziationsgrade als selbstverständlich ausgelassen. Dasselbe gilt für die nur als scheinbar anzusprechende Dissoziationskonstante der Schwefelsäure (die bei wechselnder Konzentration durchaus nicht konstant ist (vergleiche die erwähnten numerischen Unterschiede verschiedener Quellen). Die Hydronium-*Konzentration* errechnet sich in Natriumbisulfat-Lösungen unter Annahme (praktisch) vollständiger Dissoziation in H^+, Na^+ und SO_4^{-2}. Da somit sehr viel Ionen in die Lösung kommen, $1\frac{1}{2}$ mal so viel wie aus HCl, und da zweiwertige Ionen kleinere Aktivitätskoeffizienten hervorrufen als einwertige, ist die Hydronium-*Aktivität* in $NaHSO_4$-Lösungen merklich geringer als in äquimolaren HCl-Lösungen.

Nun zu EECKHOUTS Messung: $0.1M$ Na_2SO_4 hat ihm gegen KCl von gleicher Ionenstärke (Konzentrationsangabe fehlt!) eine Potentialdifferenz von 28 mvolt gegeben; danach wäre im Sulfat pH = 7.48, während seine Rechnung 7.35 gab. Auch bei viel besserer Übereinstimmung läge lediglich einer der bekannten unglücklichen Zufälle vor. Bei derartigen Messungen, zumal in ungepufferten Lösungen, können Störungen und Fehler auftreten (ich spreche aus jahrelanger Erfahrung in Präzisionsmessungen), deren Ausschaltung beschrieben sein müsste, wenn ein so unglaubliches Ergebnis fundamentale Anschauungen widerlegen sollte. Ich bin gern bereit, Herrn EECKHOUT die möglichen Fehlerquellen und die Wege zu ihrer Erkennung und Ausschaltung anzugeben; der Raum von *Anal. Chim. Acta* scheint mir aber dafür zu kostbar.

Auch aus einem zweiten Grunde halte ich die Fortführung der Aussprache an dieser Stelle für unangebracht, weil nämlich EECKHOUT zur Widerlegung meiner Anregungen Behauptungen widerlegt, die niemand aus ihnen ableiten kann. Es lässt sich nicht gegen meine Erweiterung des Ampholytbegriffes gelten machen, dass er in der Anwendung auf $NaHSO_4$ zu unsinnigen Ergebnissen führt, denn $\text{pH} = \frac{1}{2}\ (pK_1 + pK_2)$ setzt zwei messbare, endliche Gleichgewichtskonstanten voraus, und selbst EECKHOUT gesteht zu, dass hier die eine infinit $\gg 1$ ist (in Wirklichkeit sind es beide). — $(NH_4)_2HPO_4$ kann nach meinen Anschauungen nicht als Ampholyt angesprochen werden, denn in seinen Lösungen sind ***drei*** Konstanten im Spiel. — Niemand darf von *Näherungs*formeln verlangen, dass sie in extremen Verdünnungen gelten, und wenn Na_2HPO_4 nach meinen Anschauungen, die ich für begriffsklärend halte, als Ampholyt anzusprechen ist, so verliert es diesen *Character* nicht dadurch, dass die Näherungsformel in $0.001M$-Lösung nicht mehr gilt.

Literatur S. 493.

ZUSAMMENFASSUNG

In $NaHSO_4$-Lösungen der molaren Konzentration C haben wir die Hydronium-*Konzentration* $h = C$ und in Na_2SO_4-Lösungen $h = oh = 10^{-7}$. Weder EECKHOUTS Rechnungen noch seine Messung sind ein Gegenbeweis, denn in den ersten vernachlässigt er die Eigenschaften der starken Elektrolyte und in der zweiten mögliche Fehlerquellen.

SUMMARY

In $NaHSO_4$ solutions of the molar concentration C we have the hydronium *concentration* $h = C$ and in Na_2SO_4 solutions $h = oh = 10^{-7}$. Neither EECKHOUT's calculations nor his assay prove the contrary because in the former he neglects the properties of strong electrolytes and in the latter possible sources of errors.

RÉSUMÉ

Dans les solutions de $NaHSO_4$ à la concentration molaire C, on a une concentration en hydronium $h = C$ et dans les solutions de Na_2SO_4, $h = oh = 10^{-7}$. Les valeurs calculées et mesurées par EECKHOUT ne réfutent pas ces faits, puisqu'il néglige les propriétés des électrolytes forts et les sources d'erreurs possibles.

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Eingegangen den 9. Dezember 1953

V. INTERNATIONALES KOLLOQUIUM FÜR SPEKTROSKOPIE

Verein Österreichischer Chemiker
Arbeitsgruppe für
Spektrochemie und Kolorimetrie

Wien, im Dezember 1953

RUNDSCHREIBEN

Das V. Internationale Kolloquium für Spektroskopie findet laut Beschluss des IV. internationalen Treffens in Österreich statt.

Der Verein Österreichischer Chemiker hat die Arbeitsgruppe für Spektrochemie und Kolorimetrie unter ihrem Obmann, Herrn Prof. Dr. F. X. MAYER, mit der Organisation und Vorbereitung betraut. Als Sekretäre werden die Herren Dr. K. H. SPITZY und Dipl. Ing. H. SVEJDA tätig sein.

Als Tagungsort wird Gmunden im Salzkammergut (Oberösterreich) vorgeschlagen. Dieser Ort besitzt die für eine wissenschaftliche Konferenz nötige Atmosphäre und Umgebung. Er liegt zwar etwas abseits der Hauptstrecke, ist aber leicht mit Bahn und Auto erreichbar. Daneben ist seine landschaftliche Lage hervorragend geeignet, die nach den Vorträgen notwendige geistige Ausspannung zu geben. Ebenso ist die in Oberösterreich beheimatete Industrie (Eisen, Schwerchemikalien, Leichtmetall, Salinen, usw.) für Exkursionen leicht zugänglich. Als Tagungszeit ist der Termin zwischen 30. August und 3. September 1954 in Aussicht genommen, um einerseits dem Brauch, das Kolloquium stets im September abzuhalten, zu entsprechen, andererseits mit massgeblichen wissenschaftlichen Veranstaltungen der benachbarten Länder nicht zu kollidieren.

Die Gepflogenheit des Kolloquiums, sowohl die Molekularspektroskopie als auch die Emissionsspektroskopie zu behandeln, beide aber durch einen Exkursionstag in der Mitte der Veranstaltung zu trennen, soll grundsätzlich beibehalten werden.

Um Richtlinien im Sinne der Einheitlichkeit der Arbeiten und damit des Kolloquiums zu geben, wird vorgeschlagen:

1) die Anwendung der *Molekül-Spektroskopie* für die Untersuchung technischer Kunstfasern bevorzugt zu behandeln; im UR vorwiegend der nicht dispersiven UR-Spektroskopie breiten Raum zu geben.
2) In der *Emissionsspektroskopie* empfehlen wir vor allem die Analytik der Nichtleiter und der Buntmetalle betont zu besprechen.

Als Neuerung wird weiters vorgeschlagen: Das Vortragsprogramm schliesst eine Stunde früher. In der so gewonnenen Zeit sollen ein Referent und Coreferent zusammenfassend ganz kurz über ihre Erfahrungen und über Arbeiten verschiedener Autoren derselben Arbeitsrichtung berichten und sie einander gegenüberstellen. Um verständlich zu machen, was gemeint ist, seien zwei Beispiele gegeben: Es könnte ein Referent und Coreferent, die entsprechende *persönliche* Erfahrungen auf diesem Gebiet aufweisen, z.B. die Ergebnisse mit dem Kohlerohrofen nach Preuss, mit der Doppelbogenmethode nach Ahrens und der Elektrode für leicht flüchtige Stoffe nach Kaiser (s. Zschr. f. Erzmet. 1952) vergleichen, andere über Erfahrungen bei der Spurensuche mit dem Gleichstrombogen, constant-current-arc, sowie Glimmschichtmethode und globule-arc-Methode berichten. Diese kurze Berichterstattung soll die Anregung zu anschliessendem ungezwungenem Austausch persönlicher Meinungen und Erfahrungen geben. Wir glauben, dass diese Anregung dem Zwecke des Kolloquiums sehr förderlich sein wird.

Auch hier wollen wir im Sinne der Einheitlichkeit der Vorträge Richtlinien vorschlagen, von denen wir glauben, dass sie Allgemeininteresse besitzen und zwar bezüglich der *Molekularspektroskopie*

a) kritische Gegenüberstellung lichtelektrischer und photographischer Methoden,
b) UR- und Raman-Spektroskopie als analytisches Hilfsmittel;

bezüglich der *Emissionsspektroskopie*

a) Auswertung der Spektrogramme,
b) Erfahrungen über leitprobenfreie Verfahren, die in Richtung der Arbeiten von HARVEY, constant-temperature-arc von Addink u.a. gehen.

An Exkursionen sind geplant: Besichtigung der oberösterreichischen Eisen- und Aluminiumindustrie, allenfalls der Salinen und nicht zuletzt der landschaftlichen Schönheiten des Salzkammergutes (Dachsteineishöhlen!). Die letzteren Exkursionen können auf Wunsch auch vor und nach dem Kolloquium arrangiert werden.

Für die Tagung wird der Theatersaal samt Projektionseinrichtungen zur Verfügung stehen. Die Unterbringung wird in Hotels zu drei verschiedenen Preislagen erfolgen. Um die Aufenthaltskosten zu erniedrigen, ist beabsichtigt, bei entsprechender vorheriger Anmeldung gemeinsame Mahlzeiten einzurichten.

Genügendes Interesse vorausgesetzt, wird ein reichhaltiges Damenprogramm, wie Seerundfahrten, Seilbahnfahrt auf den Feuerkogel, Besuch von Ischl etc., vorbereitet werden.

Um die Organisation des Kolloquiums zu erleichtern und einen reibungslosen Verlauf zu ermöglichen, ersuchen wir die zuständigen Organisationen in den einzelnen Ländern um ihre Mitwirkung.

Wir schlagen vor:

1) die Länderorganisationen (LO) übernehmen in ihrem Bereich die Werbung für das Kolloquium, indem sie entweder bei uns Rundschreiben, bzw. Einladungen in entsprechender Menge zur Verteilung im eigenen Wirkungskreis anfordern

oder zumindest eine vollständige Adressenliste der Fachkollegen übermitteln. Nationen, deren LO uns nicht bekannt ist, ersuchen wir um Bekanntgabe der daran interessierten Fachkollegen.

2) Wir ersuchen die LO, eine Sichtung der eingereichten Vorträge im Sinne der genannten Richtlinien vorzunehmen. Um einerseits dem von Jahr zu Jahr steigendem Interesse weitester Kreise am Kolloquium gerecht zu werden, andererseits aber eine Benachteiligung einzelner Länder hintanzuhalten, erlauben wir uns vorzuschlagen, je Land die Zahl der eingereichten Vorträge mit fünf zu begrenzen. Wegen der Fülle der zu erwartenden Vorträge empfehlen wir die Vortragszeit mit 15 Min. anzusetzen. Die endgültige Auswahl und Zusammenstellung des Vortragsprogrammes werden wir wohl übernehmen müssen.

Es ist beabsichtigt, auch diesmal Kurzberichte der Vorträge in den drei Kongreßsprachen zu überreichen. Damit dies rechtzeitig geschehen kann, ersuchen wir die LO, uns diese Kurzberichte im Ausmass von maximal zwei Schreibmaschinenseiten bis spätestens 30.5. 1954 zukommen zu lassen. Auch müssen wir darauf hinweisen, dass es wegen des internationalen Charakters der Tagung wünschenswert ist, sich beim Diamaterial an die internationalen Normen (8.5 × 10 bzw. 5×5 cm) zu halten und dasselbe mindestens zweisprachig zu beschriften. Es hat sich gezeigt, dass es in der Regel genügt, für die Diskussionen Dolmetscher in Anspruch zu nehmen. Es wird vorgesorgt werden, dass den verschiedensprachigen Teilnehmern des Kolloquiums Dolmetscher für die drei Kongresssprachen zur Verfügung stehen.

Stellungnahme zu unseren Vorschlägen und Anregungen bitten wir ehebaldigst, spätestens jedoch bis *Ende März 1954 an die Arbeitsgruppe für Spektrochemie und Kolorimetrie im VöCh, Wien, IX., Sensengasse 2 (Institut für geriehtliche Medizin Tel. A 28-5-50/Kl. 405 zu richten.*

Für die Arbeitsgruppe
Prof. Dr. F. X. Mayer e.h.
Dipl. Ing. H. Svejda e.h. Dr. K. H. Spitzy e.h.

SUMMARY

The fifth International Colloquium for Spectroscopy takes place at Gmunden (Salzkammergut, Austria) and will last from August 30th till September 3rd, 1954.

The subdivision in absorption and emission spectroscopy will be kept as usual. It is suggested to deal preferably with the application of the molecule spectroscopy to the examination of technical artificial fibres; in the case of the emission spectroscopy we recommend to discuss chiefly the analysis of non-conductors and the alloys of copper.

In addition to the lectures, discussion evenings will be arranged at which one or more reporters will give an account of personal experiences.

The organisations of the countries are asked to hand in no more than five lectures (15 minutes) by May 30th, 1954, at the latest.

It is requested that expressions of opinion concerning these suggestions be sent to the above-mentioned address.

RÉSUMÉ

Le cinquième colloquium international de spectroscopie aura lieu à Gmunden (Salzkammergut, Autriche) du 30 août au 3 septembre 1954. La subdivision en spectroscopie d'absorption et d'émission sera conservée comme précédemment. On propose d'appliquer de préférence la spectroscopie moléculaire à l'examen des fibres artificielles techniques. En ce qui concerne la spectroscopie d'émission, on recommande de discuter de l'analyse des non-conducteurs et des alliages de cuivre. A côté de ces communications, seront organisées des séances de discussions durant lesquelles une ou plusieurs personnes parleront de leurs expériences personnelles. Chaque pays pourra présenter au maximum 5 communications, (d'une durée de quinze minutes). Elles devront nous parvenir jusqu'au 30.V.1954 au plus tard.

Prière de bien vouloir faire part des avis concernant les propositions faites, à l'adresse mentionnée ci-dessus.

THE SOCIETY FOR ANALYTICAL CHEMISTRY

(Formerly the Society of Public Analysts and Other Analytical Chemists)

Annual General Meeting of the Society

The Eightieth Annual General Meeting of the Society was held on Wednesday, March 3rd, 1954, in the Meeting Room of the Royal Society, Burlington House, London, W.1, with the President, Dr. D. W. KENT-JONES, F.R.I.C., in the Chair. The Financial Statement and Report of the Council for the past year were submitted and approved. The membership of the Society was now 1646, an increase of 54 over last year. The Society has held eight Ordinary Meetings during the year, six in London (one organized by the Microchemistry Group), one in Glasgow (organised jointly by the Scottish Section and the Microchemistry Group) and one in Southampton (organised by the Physical Methods Group). In addition a Joint Meeting was held in London with the Royal Institute of Chemistry. Eighteen meetings were held by the Society's Sections and Groups. A Humble Address of congratulations was presented to Her Majesty on the occasion of her Coronation in June, 1953, and this address was graciously received and acknowledged.

The following Officers and Members of Council were elected for the forthcoming year — *President:* D. W. KENT-JONES. *Past Presidents serving on the Council:* LEWIS EYNON, G. W. MONIER-WILLIAMS, J. R. NICHOLLS and G. TAYLOR. *Vice-Presidents:* C. A. ADAMS, A. J. AMOS and T. MCLACHLAN. *Honorary Treasurer:* J. H. HAMENCE. *Honorary Secretary:* K. A. WILLIAMS. *Other Members of Council:* D. C. M. ADAMSON, A. L. BACHARACH, R. C. CHIRNSIDE, Miss M. CORNER, D. C. GARRATT, J. HASLAM C. L. HINTON, H. W. HODGSON, H. M. N. H. IRVING, A. G. J. LIPSCOMB, R. E. STUCKEY and C. WHALLEY. *Ex-Officio Members:* T. W. LOVETT (Chairman of the North of England Section), R. S. WATSON (Chairman of the Scottish Section), A. M. WARD (Chairman of the Microchemistry Group), A. A. SMALES (Chairman of the Physical Methods Group) and L. J. HARRIS (Chairman of the Biological Methods Group). *Honorary Assistant Secretary:* N. L. ALLPORT.

The Annual General Meeting was followed immediately by the Bernard Dyer Memorial Lecture given by Dr. E. B. HUGHES, F.R.I.C., and entitled *The Contribution of Public Analysts and Other Analytical Chemists to Public Welfare.*

Dr. HUGHES said that the analyst had chosen a career that necessitated careful and accurate work, requiring the application of any scientifically controllable means of pursuing an enquiry. Analysis was not merely the handmaiden of industry — although it was sometimes regarded as the Cinderella of industry — it was essential both for control and for research.

Much had been learnt about the effects of trace elements on plants, but less was known of the effect of the beneficial trace elements on humans. The use of chemical pesticides led to anxiety about the possible effects of their residues on crops. These problems were even more urgent than the precise specification of known methods of analysis to meet the requirements of standards and limits of contaminants in foods.

Without analysis in the manufacturing industries, rule of thumb would be the only guide, and faulty products and irregular quality would be commonplace instead of rare. The key position occupied by analysts in every industry was worthy of wider recognition. It had been said that when trade became bad, the laboratory staff should be doubled, and the same was true in the present paramount need for expansion of trade. Dr. HUGHES suggested a Symposium on Analysis in Science and Industry to describe what analysts did rather than how they did it. He emphasized that industry, the Trade Associations, the economists and the Government must be told something of the study and zeal that lay largely hidden from them, in the analysts' contribution to the prosperity of industry and of the Nation.

Dr. HUGHES then referred to the work of the public analysts, with whom food chemists had much in common. The first Food and Drugs Act of 1872 was only implemented because there were in practice a few analysts who had the wisdom and foresight to unite to share their knowledge, and they formed in 1875, the Society of Public Analysts. It was common, in referring to the Act of 1872, to relate harrowing stories of openly fraudulent and sometimes harmful adulteration of food in the early 19th century, but even then there were in existence food manufacturing firms whose names were still household words and who were as honourable then as now. Although those days were past, and Public Analysts' work was now more prosaic, it was still essential for the detection of the infringement of standards and regulations.

The manufacturer needed more stringent testing of his raw materials than was required by the Food and Drugs Act. He must not leave anything to chance, and although analysis showed samples to be generally satisfactory, the occasional faulty sample must be looked for.

A markable, effective and just Food and Drugs Act was necessary to protect the public and to guide the responsible manufacturer. The Minister of Food had widely and generously interpreted the requirement in the 1938 Act that he should consult with representative organisations as he thought fit. The new Food and Drugs Amendment Bill appeared to imply much more control, but much could be gained from clearly stated needful and useful Regulations. If methods of analysis were to be prescribed, it was to be hoped that they would be approved and preferably produced by this Society, and that they would be subject to review as circumstances required.

He was glad to pay a tribute to Public Analysts for their co-operation with food chemists. The Public Analysts had relinquished their claim on the name of the Society and had generously accepted the changes necessitated by the many and expanding interests of the Society. In the new Association of Public Analysts it was to be hoped they would find all the professional status and recognition that was their due, but above all it was hoped that they would continue to support this Society and maintain their close scientific contact with the food chemists.

In this age of manufactured food, supplied to countryman and townsman alike, the objective of the food chemist was to ensure that it should be wholesome, nutritive, attractive and pleasing, and capable of withstanding the exigencies of distribution. Their first duty was to maintain, and if possible to enhance, the reputation of their firm's goods. In this respect the food chemist — one of the "other analytical chemists" — was as much, perhaps more, a contributor to public welfare than was the Public Analyst; more so, because his object was not merely to find evidence of harm or infringement of law or regulation, but definitely to prevent such mischance. To a food chemist a raw material must not only be genuine or pure, it must also have other qualities or characteristics of importance in its intended use. Constant application of analysis and microbiological examination, detailed specification of the care required in manufacturing processes, advice on packing, and tests and inspections to verify the observance of these specifications, was essential.

During such intensive examination, data that would not come to light in casual inspection become available. The care that a food manufacturer took to avoid contamination be naturally required also of the suppliers of the raw materials, and in this alone there was a public benefit.

In recent years the food chemist had been called the Food Technologist. This should indicate one whose postgraduate training had been concerned with food and food manufacture, and in the speaker's opinion the analyst, suitably experienced, was the ideal food technologist. However, he should not be restricted to the laboratory bench: he should know something of the functioning of the industrial plant and, when he had special knowledge, he should consult and work with the engineer, designer and architect.

The Ethics of the chemist in the food industry must be referred to. It had been suggested that the food manufacturer, for convenience and for profit, made use of "chemicals", guided by his food technologists, to the consequent detriment of the consumer. Much had been published to show how far this was from the truth. In fact, a joint request had been made by this Society and the Food Group of the Society of Chemical Industry to the Ministry of Food to review the Preservative Regulations, and a Committee had been formed with terms of reference including not only preservatives but also other chemical additives. It was to be hoped that an unsatisfactory aspect of this subject, the variation between countries as to what was suitable and the amount permitted, would one day be put right by international co-operation.

At the conclusion of the Meeting, the President presented the Bernard Dyer Memorial Medal to Dr. E. B. HUGHES.

The Meeting was followed by an informal Dinner, at the Trocadero Restaurant, at which the guests of honour were Dr. E. B. HUGHES, F.R.I.C. and Mrs. HUGHES, and Professor Sir CHARLES DODDS, M.V.O., D.Sc., Ph.D., M.D., F.R.C.P., F.R.I.C., F.R.S.E., F.R.S. and Lady DODDS.

BOOK REVIEWS

Applied Electron Microscopy by R. B. FISCHER. Indiana University Press, 1953. XIII + 234 pages, 87 Fig.

The aim of this book is to provide a general understanding of the principles of electron microscopy and an acquaintance with the types of things the instrument can do; it is directed mainly to those who are not practising microscopists. The principles are covered in four chapters including an introduction (largely definitive). In these chapters the theory of electron optics is dealt with in a simplified, but nevertheless satisfactory manner. The design and construction of the various components of the electron microscope is dealt with in the course of about 50 pages with short descriptions of a number of commercial models and a brief appraisal of their potentialities. The techniques and applications of electron microscopy are described in five chapters with adequate practical detail of film support, shadow casting, etc. to convince the general reader of the essential art of electron microscopy. This is followed by an interesting and informative chapter on special methods which reveal the scope and power of the instrument. The final chapter contains short descriptions of allied instruments, *e.g.* emission and proton microscopes with a brief account of their applicability in various fields. Although the general lay-out of the book falls below the standards one has come to associate with American publication, the illustrations, both in their choice and reproduction, are very good. The book should provide much of interest to those who move on the fringe of the field of electron microscopy.

G. M. BURNETT (Birmingham)

Substances naturelles de synthese — Volume VII, par A. Allais, J. Mathieu, A. Petit, P. Poirier et L. Velluz. Masson et Cie, Paris, 1953. Une brochure de 157 pages et 2 planches hors-texte.

Une partie importante du fascicule (36 pages) est occupée par la synthèse de la cortisone, avec en annexe, celle de l'adrénostérone; puis vient la préparation de la D + L hydroxyproline selon LEUCHS et celle de l'α-irone, en collaboration avec le Dr. Y. Naves, la lyxoflavine et le L(+)-lyxose, la D+L proline et la stachydrine. Comme méthodes générales, on cite la cyclisation pyrrolique en vue de la synthèse d'importants pigments naturels et l'on donne en tableaux des exemples de telles cyclisations réellement effectuées. In en est de même avec la cyclisation indolique avec applications particulières à la série des sucres. Les treize dernières pages sont occupées par la liste des indicateurs de pH (colorés et de phosphorescence) avec leur formule, leur zone de virage et la composition de la solution à utiliser.

J'ai déjà dit beaucoup de bien de cette collection dont on attend avec impatience les différents épisodes comme ceux des romans d'aventures à grand succès. Il s'agit bien là en effet d'aventures dans un domaine tout récemment exploré et le succès est déjà acquis grâce à la compétence indiscutable des auteurs, au choix heureux des sujets choisis et à la présentation matérielle irréprochable.

Clément Duval (Paris)

Analyse der Metalle. Herausgegeben vom Chemikerausschuss der Gesellschaft Deutscher Metallhütten- und Bergleute e.V. II. Bd.: *Betriebsanalysen.* In zwei Teilen. Mit je 174 Abbildungen. 1. Teil: XI, 716 Seiten; 2. Teil: IV, 706 Seiten Gr.—8°, 1953. Ladenpreis: Ganzleinen in 2 Bd. geb. DM 114 —.

Cet ouvrage fait partie d'une série de publications sur l'analyse des métaux et présente un recueil de méthodes analytiques utilisées avec succès dans l'industrie métallurgique allemande. Toutes ces méthodes sont donc basées sur une longue expérience industrielle et permettent d'obtenir des résultats rapides, chose indispensable dans le contrôle de fabrication. Certaines entreprises de la métallurgie allemande possèdent des laboratoires modernes et bien équipés; d'autres ne disposent que de moyens plus primitifs. C'est pourquoi les méthodes indiquées dans cet ouvrage sont très diverses, mais les auteurs tiennent toujours compte de certains facteurs importants comme: durée d'analyse, précision, source d'erreurs et les moyens de les éviter; on y trouve de nombreuses références bibliographiques.

La plus grande partie de l'ouvrage est consacrée à l'analyse des éléments, classés par ordre alphabétique. Pour chaque élément on indique sa provenance, quelques réactions caractéristiques, puis les méthodes d'analyse des minerais correspondants et de tous les produits que l'on obtient au cours des opérations industrielles concernant l'élément en question; enfin, on y trouve les méthodes d'analyse du métal pur, de ses oxydes, de ses sels et tous les alliages courants.

Un chapitre important est consacré à l'analyse de toutes les matières qui peuvent intéresser le métallurgiste, tels que matériaux de construction, combustibles, eaux, gaz, produits secondaires, déchets, etc.

Les derniers chapitres, comprenant une centaine de pages, sont consacrés aux méthodes d'analyse physico-chimique, telles qu'on les applique dans l'industrie. Dans l'introduction de chacune de ces méthodes, on trouve un exposé des bases théoriques et la description détaillée des appareils en usage. La photométrie a été particulièrement bien décrite et un grand nombre d'appareils existants y sont cités.

A la fin du deuxième volume il y a un chapitre sur la préparation de certaines solutions courantes; sur la solubilité des sels les plus utilisés, sur les indicateurs et leur emploi, sur la normalisation des métaux et de leurs alliages.

Nous recommandons vivement ce remarquable ouvrage aux chimistes et aux techniciens.

Z. Besso (Genève)

OXIDATIONS AND REDUCTIONS OF IRON-CYANOGEN COMPOUNDS OF COBALT, NICKEL, CADMIUM AND ZINC

by

MORITZ KOHN*

WERNER[1] found that cobalt ferrocyanide is oxidized by bromine water to cobalt ferricyanide and the latter by an excess of bromine water to cobaltic hydroxide. However, it was observed that by cautious oxidation with bromine water or with nitrous acid or with hydrogen peroxide in presence of acids, cobalt Prussian blue (cobalt ferroferricyanide)[2] is produced. In the reaction with nitrous acid 0.0001 g nitrous acid in one drop of water if mixed with one drop of a suspension of cobalt ferrocyanide gives a distinct blue coloration. Cobalt ferricyanide can be reduced by sulfurous acid in presence of hydrochloric acid to cobalt Prussian blue. Nickel ferrocyanide is oxidized by bromine water, by nitrous acid or by hydrogen peroxide in the presence of acids to nickel ferricyanide, while nickel ferricyanide is reduced by sulfurous acid to nickel ferrocyanide. Cadmium ferrocyanide is also oxidized by bromine water to cadmium ferricyanide, while cadmium ferricyanide and zinc ferricyanide are reduced by sulfurous acid to the ferrocyanides. To the cobalt Prussian blue (cobalt ferroferricyanide) was assigned the composition[2]: $6Co_2[Fe(CN)_6].Co_3[Fe(CN)_6]_2$. This formula was computed under the assumption that in the reaction with potassium ferrocyanide no potassium ferrocyanide was retained by the blue substance. This reaction with potassium ferrocyanide was necessary for the determination of the ferricyan. Future investigations will try to answer this question definitely. Moreover it was pointed out in the former paper how difficult and how doubtful it is to compute formulae of iron-cyanogen compounds on the basis of analytical determinations.

Oxidation of cobalt ferrocyanide to cobalt Prussian blue

By bromine water

The quantity of bromine water used in this experiment corresponds to the afore-mentioned composition of the cobalt Prussian blue. 17 ml 0.1*M* cobalt chloride and 8 ml 0.1*M* $K_4[Fe(CN)_6]$ were mixed and 0.5 ml bromine water which was diluted with 7.5 ml water were added. The mixture was shaken. A blue precipitate settles after some time.

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By nitrous acid

A sodium nitrite solution containing 0.0040 g $NaNO_2$ in 1 ml water was used.

a. 1.5 ml 0.1*M* cobalt chloride were precipitated with 0.5 ml 0.1*M* potassium ferrocyanide and 5 ml water were added. 2.5 ml 0.1*N* HCl were mixed with 2.5 ml of the sodium nitrite solution. These 5 ml of the acid-nitrite solution and the solution containing the precipitated cobalt ferrocyanide were combined. The blue color appeared.

b. One drop of a suspension of cobalt ferrocyanide (prepared by mixing of 1.5 ml 0.1*M* cobalt chloride and 0.5 ml 0.1*M* potassium ferrocyanide) was combined on a watch glass with one drop of the acid-nitrite mixture (containing about 0.0001 g HNO_2) used in a. The blue color appeared immediately.

By hydrogen peroxide

a. In presence of hydrochloric acid:

One drop of perhydrol was diluted with 20 ml water and 10 ml 0.1*N* HCl were added afterwards. A suspension of cobalt ferrocyanide was prepared by precipitation of 2.25 ml 0.1*M* cobalt chloride with 1 ml 0.1*M* potassium ferrocyanide. It was sufficient to add 6.5 ml of the hydrochloric acid-hydrogen peroxide mixture to the cobalt ferrocyanide to produce the grayish ultramarine blue product of the oxidation.

b. In presence of sulfuric acid:

1 ml perhydrol was diluted to 10 ml; 1 ml sulfuric acid was diluted to 10 ml. These solutions were mixed. 3 ml 0.1*M* cobalt chloride were precipitated with 1 ml 0.1*M* potassium ferrocyanide. The addition of 2 ml of the mixture of hydrogen peroxide and sulfuric acid produced the blue product of the oxdiation.

Reduction of cobalt ferricyanide to cobalt Prussian blue by sodium sulfite

2.2 ml 0.1*M* cobalt chloride were precipitated with 1.33 ml 0.1*M* potassium ferricyanide. By addition of 2 ml 10% sodium sulfite the purple red cobalt ferricyanide turns to a light brownish color. If 0.1*N* HCl is added to a volume of 10 ml now, the color does not change essentially, but the precipitate settles. Even heating does not produce a change. But if 10 ml HCl (1:1) are added and heated the precipitate becomes bluish. If 4 ml of the sulfite solution are added now and the mixture is heated, the grayish ultramarine blue cobalt ferroferricyanide is formed.

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Oxidation of nickel ferrocyanide to nickel ferricyanide

By bromine water

15 ml 0.1*M* $NiCl_2$ were precipitated with 6 ml 0.1*M* potassium ferrocyanide. By addition of a mixture of 2 ml bromine water and 8 ml water nickel ferricyanide is formed.

By nitrous acid

4 ml 0.1*M* $NiCl_2$ were precipitated with 1.5 ml 0.1*M* potassium ferrocyanide. 10 ml of a solution of sodium nitrite containing 0.05 g $NaNO_2$ were mixed with 12 ml 0.1*N* HCl. By addition of the hydrochloric acid-sodium nitrite mixture to the suspension of nickel ferrocyanide yellow nickel ferricyanide resulted.

By hydrogen peroxide

a. in presence of hydrochloric acid:
23.5 ml of a hydrogen peroxide-hydrochloric acid mixture of the same composition that was used for the oxidation of the cobalt ferrocyanide were added to a precipitate prepared by mixing of 2.25 ml 0.1*M* $NiCl_2$ with 1 ml 0.1*M* potassium ferrocyanide. Nickel ferricyanide was formed.

b. in presence of sulfuric acid:
2.25 ml 0.1*M* nickel chloride were precipitated with 1 ml 0.1*M* potassium ferrocyanide. The addition of 5 ml of a mixture of hydrogen peroxide and sulfuric acid of the same composition which was used for the oxidation of cobalt ferrocyanide produced nickel ferricyanide.

Reduction of nickel ferricyanide to nickel ferrocyanide by sodium sulfite

Nickel ferricyanide prepared by precipitation of 1.33 ml 0.1*M* potassium ferricyanide with 2 ml 0.1*M* nickel chloride is reduced to nickel ferrocyanide immediately on addition of 2 ml 10% sodium sulfite.

By sodium sulfite in presence of hydrochloric acid

If to a precipitate of nickel ferricyanide prepared as afore-mentioned a mixture of 8 ml 0.1*N* HCl and 2 ml 10% sodium sulfite is added the reduction to the green nickel ferrocyanide proceeds in a few minutes. But if a mixture of 3 ml concentrated hydrochloric acid 5 ml water and 2 ml 10% sodium sulfite is added no reduction takes place.

Oxidation of cadmium ferrocyanide to cadmium ferricyanide by bromine water

22 ml 0.1M cadmium chloride were precipitated with 10 ml 0.1M potassium ferrocyanide. 4 ml bromine water which were diluted with 10 ml water were added and the mixture was shaken. The yellow precipitate was filtered after twenty-four hours and washed with water in order to remove the excess of cadmium chloride and the excess of bromine. The precipitate was washed off into a beaker. 20 ml 0.1M potassium ferrocyanide and 15 g sodium chloride were added. When the cadmium ferrocyanide had settled, it was filtered through the original filter and washed thoroughly with water. The combined filtrates used up 8.74 ml 0.1N sodium thiosulfate. Therefore 87.4% of the ferrocyanide was oxidized.

Reduction of cadmium ferricyanide to cadmium ferrocyanide by sulfurous acid

I. 3 ml 0.1M cadmium chloride were diluted with 5 ml water and this solution precipitated with 2 ml 0.1M potassium ferricyanide. The addition of 3 ml 10% sodium sulfite produced the formation of white cadmium ferrocyanide.

II. The same quantities as used in I. The addition of a mixture of 3 ml 10% Na_2SO_3 and 7 ml 0.1N HCl yielded pure white cadmium ferrocyanide.

Reduction of zinc ferricyanide to zinc ferrocyanide by sulfurous acid

The reactions were carried out in the same way as in the case of cadmium. But instead of 3 ml 0.1M cadmium chloride 3 ml 0.1M zinc sulfate were used. White zinc ferrocyanide was formed.

SUMMARY

I. Cobalt ferrocyanide is oxidized by bromine water, by nitrous acid or by hydrogen peroxide in presence of acids to cobalt ferroferricyanide (cobalt Prussian blue), while cobalt ferricyanide is reduced by sulfurous acid to cobalt Prussian blue.

II. Nickel ferrocyanide is oxidized by nitrous acid or by hydrogen peroxide in presence of acids to nickel ferricyanide.

III. Nickel ferrocyanide and cadmium ferrocyanide are oxidized by bromine water to the ferricyanides.

IV. The ferricyanides of nickel, cadmium and zinc are reduced by sulfurous acid to the ferrocyanides.

RÉSUMÉ

I. Le ferrocyanure de cobalt est oxydé par l'eau de brome, par l'acide nitreux ou par le peroxyde d'hydrogène en solution acide, en ferroferricyanure de cobalt (bleu de Prusse cobaltique), tandis que le ferricyanure de cobalt est réduit par l'acide sulfureux en bleu de Prusse cobaltique.

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II. Le ferrocyanure de nickel est oxydé par l'acide nitreux ou par le peroxyde d'hydrogène en solution acide, en ferricyanure de nickel.

III. Le ferrocyanure de nickel et le ferrocyanure de cadmium sont oxydés par l'eau de brome en ferricyanures.

IV. Les ferricyanures de nickel, de cadmium et de zinc sont réduits par l'acide sulfureux en ferrocyanures.

ZUSAMMENFASSUNG

I. Kobaltferrozyanid wird durch Bromwasser, durch salpetrige Säure oder durch Wasserstoffsuperoxyd in Gegenwart von Säuren zum Kobaltferroferrizyanid (Kobalt Berliner Blau) oxydiert, während Kobaltferrizyanid durch schweflige Säure zum Kobaltberlinerblau reduziert wird.

II. Nickelferrozyanid wird durch salpetrige Säure, sowie durch Wasserstoffsuperoxyd in Gegenwart von Säuren zum Nickelferrizyanid oxydiert.

III. Nickelferrozyanid und Kadmiumferrozyanid werden durch Bromwasser zu den Ferrizyaniden oxydiert.

IV. Die Ferrizyanide des Nickels, Kadmiums und Zinks werden durch schweflige Säure zu den Ferrozyaniden reduziert.

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BEITRÄGE ZUR MORPHOLOGIE DES NACH DEM L. W. WINKLER'SCHEN VERFAHREN HERGESTELLTEN $BaSO_4$-NIEDERSCHLAGES

von

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Die Verwendung von Ammonchlorid als Hilfsmittel in der gravimetrischen Analyse ist allgemein verbreitet, obwohl der Grund für seinen Gebrauch nicht immer klar herausgestellt wird. Dies trifft besonders für die Verwendung von NH_4Cl bei der $BaSO_4$-Fällung zu.

Ein besonders wichtiger Gesichtspunkt ist hierbei, dass der Niederschlag so beschaffen sein muss, dass er sich ohne irgendeine Veränderung der stöchiometrischen Zusammensetzung gut filtrieren lässt. Diesbezügliche Versuche von PAIS[1] ergaben, dass der in Gegenwart von Ammonchlorid nach der WINKLER'schen Vorschrift[2] bei $pH = 2$ gefällte $BaSO_4$-Niederschlag nur Spuren von Ammoniak enthält. Nur grössere Mengen von NH_4Cl verursachten infolge erhöhter Löslichkeit des Bariumsulfates Minderwerte in der Sulfatanalyse. Die WINKLER'schen $BaSO_4$-Niederschläge zeichnen sich durch besonders schnelles Absetzen und gute Filtrierbarkeit — sie können durch Jenaer Sinterglasfilter G.3 filtriert werden — aus. Sie erreichen Gewichtskonstanz nach dem Waschen mit Wasser und absolutem Alkohol innerhalb 10-20 Minuten, wenn ein starker Luftstrom durchgesaugt wird. Das Gewicht ändert sich nicht, wenn der Niederschlag nachher bei 130° weiter getrocknet wird[3].

Bei der Fällung von Niederschlägen üben die anwesenden Fremdstoffe, in unserem Fall die Elektrolyte auf die Ausbildung der Niederschlagskörnchen (Kristalle) einen nicht zu unterschätzenden Einfluss aus, welch letzterer sich besonders in der Morphologie des Niederschlages erkennen lässt.

Es wurden also von uns morphologische Versuche angestellt, wobei die teils in Gegenwart, teils in Abwesenheit von NH_4Cl gefällten $BaSO_4$-Niederschläge elektronenmikroskopisch, bzw. lichtmikroskopisch untersucht wurden.

BESCHREIBUNG DER VERSUCHE

Elektronenmikroskopische Versuche. Aus etwas 10^{-4}.*M*-er $BaCl_2$-Lösung wurde das $BaSO_4$ mit äquivalenten Mengen etwa 10^{-4}.*M*-er H_2SO_4-Lösung in der

Literatur S. 509.

Siedehitze bei etwa pH = 2 teils in Abwesenheit (Versuchsreihe „A"), teils in Gegenwart (Versuchsreihe „B") von 1 bzw. 2% Ammonchlorid (der %-Gehalt bezieht sich g per Endvolum der Versuchslösung in ml) aus 50 ml Lösung gefällt. Es wurden aber auch Versuche angestellt, in welchen das Ba^{+2}-Ion bzw. SO_4^{-2}-Ion im Überschuss der Reaktionslösung zugegeben wurde. Die Reihenfolge der Reagenzien ergab nach unseren Versuchen keinen bemerkbaren Einfluss. In der Versuchsreihe „A" waren allerdings Versuche in welchen das NH_4Cl nachträglich, also nach der Fällung in der Reaktionsflüssigkeit aufgelöst wurde. Je 1 Tropfen der auf dieser Weise hergestellten niederschlaghaltigen, trüben Lösung wurde auf einem elektronenmikroskopischen Objektträger eingetrocknet und gleich bzw. nach 24 Stunden nach dem Eintrocknen im Elektronenmikroskop untersucht[4]. Aufnahmen (1AE-3AE bzw. 4BE-7BE).

Lichtmikroskopische Versuche. Aus einer etwa 100 mg $BaSO_4$ entsprechenden Menge K_2SO_4- bzw. $BaCl_2$-Lösung wurde das Sulfation, bzw. das Bariumion aus 100 ml Lösung bei etwa pH = 2 teils in Abwesenheit teils in Gegenwart von 1% Ammonchlorid genau nach der WINKLER'schen Vorschrift, als $BaSO_4$ gefällt. Der Niederschlag wurde im Lichtmikroskop untersucht und photographiert* (Aufnahmen 8AL, 9AL bzw. 10BL-12BL). Es wurden endlich Versuche gemäss der WINKLER'schen Vorschrift, aber in neutraler Lösung ausgeführt (Aufnahme 13BL).

Wir möchten ausdrücklich betonen, dass die typischen Abbildungen unserer Abhandlung aus zahlreichen Aufnahmen ausgelesen wurden.

BESPRECHUNG DER RESULTATE

Wurde das $BaSO_4$ aus etwa 10^{-4}.*M*-ren Lösungen bei pH = 2 in Abwesenheit von Ammonchlorid gefällt, so wiesen die Gebilde im Elektronenmikroskop in einer Richtung etwas verlängerte, kreuzförmige Formen auf (Aufnahmen 1AE-3AE), deren Ränder mit Spitzen besetzt waren und zwar unabhängig davon, dass in einem Versuche (Aufnahmen 2AE—3AE) Ammonchlorid nachträglich der Lösung zugegeben wurde. — Wurde die $BaSO_4$-Fällung unter denselben Verhältnissen, doch in Gegenwart von 2% Ammonchlorid vorgenommen, so zeigten die Bariumsulfatkristallbildungen mehr oder weniger regelmässige quadratische Formen mit geradlinigen Kanten.** Die Formen entstanden ganz unabhängig davon, dass in den ersten 3 Versuchen (Aufnahmen 4BE-6BE) Schwefelsäure mit einem $BaCl_2$-Überschuss, in dem 4-ten Versuch (Aufnahme 7BE) dagegen das $BaCl_2$ mit einem Schwefelsäureüberschuss als $BaSO_4$ gefällt wurde.

Die lichtmikroskopischen Aufnahmen beweisen uns nun, dass der Effekt des Ammonchlorids — obwohl die Morphologie der Kristalle sich etwas änderte — derselbe blieb, wenn die $BaSO_4$-Fällung aus etwa 10^{-2} M-en Lösungen bei pH = 2 genau nach der WINKLER'schen Methode vorgenommen wurde. So waren die Kristallgebilde mit gezackten Rändern, wenn kein Ammonchlorid bei der Fällung zugegen war (Aufnahmen 8AL-9AL) und mit geradlinigen Kanten versehen, wenn das $BaSO_4$ in Gegenwart von Ammonchlorid gefällt wurde (Aufnahmen 10BL-12BL). Es war nicht unsere Absicht den Einfluss der verschiedenen Ionen bzw. ihrer Konzentration auf die Morphologie der $BaSO_4$-Kristalle zu untersuchen. Diesbezüglich verweisen wir auf die Untersuchungen von BUZÁGH[5]. Ebenso beschäftigten wir uns nicht mit der $BaSO_4$-Füllung bei verschiedenen pH-Werten um die günstigsten Verhältnisse bezüglich Filtrierbarkeit des Niederschlages zu erfahren. ERDEY und Mitarbeiter[6], sowie FISCHER UND RHINEHAMMER[7] haben nachgewiesen, dass das Niedrighalten des pH-Wertes für die gute Filtrierbarkeit des Niederschlages einen günstigen Einfluss auf die Morphologie desselben ausübt. Aus den elektronenmikroskopischen Aufnahmen von FISCHER UND RHINEHAMMER[7] kann allerdings festgestellt werden, dass der Einfluss der Wasserstoffionenkonzentration und der des Ammonchlorids die gleiche Wirkung auf die Morphologie der $BaSO_4$-Kristalle haben. — Somit kann vorläufig für beide Effekte die gleiche Erklärung angenommen werden. Ist Säure oder Ammonchlorid in reichlicher Menge vorhanden, so wird die Assoziationsgeschwindigkeit der $BaSO_4$-Kristalle bzw. Kristallkeime infolge Adsorption von Ionen sehr zurückgedrängt. Bei hohen pH-Werten, bzw. in Abwesenheit von Ammonchlorid ist die Geschwindigkeit der Agglomeration der $BaSO_4$-Kristalle derart gross, dass die Kanten der Kristallgebilde mit Spitzen belegt werden. Wegen Brüchigkeit dieser Spitzen sind solche Niederschläge schwer zu filtrieren. Dies bestätigt besonders unsere Aufnahme 13BL, welche von einem $BaSO_4$-Niederschlag — aus neutraler Lösung, doch in Gegenwart von Ammonchlorid — nach WINKLER gefällt wurde. Die Kristalle besitzen nicht nur gezackte Ränder, sondern auch im allgemeinen auffällig dünne Gebilde.

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* Der Niederschlag wurde diesmal unter dem Lichtmikroskop untersucht, da die $BaSO_4$-Kristalle viel zu gross sind, um im Elektronenmikroskop untersucht werden zu können.

** Die Kristalle wiesen eine rhombische Struktur auf. Für die kristallographische Untersuchungen sind wir Frau V. FUX-SZÉKY und Herrn Prof. K. SZTRÓKAY zu besonderem Danke verpflichtet.

Literatur S. 509.

Man kann also die WINKLER'sche Fällungstechnik mit recht als besonders günstig betrachten.

Für die technische Mithilfe möchten die Autoren ihren wärmsten Dank Frl. K. SZIVESSY aussprechen.

ZUSAMMENFASSUNG

Verfasser haben in ihrer elektronen- bzw. lichtmikroskopischen Untersuchungen festgestellt, dass ein Ammonchloridzusatz bei der Fällung von $BaSO_4$ nach der Vorschrift von WINKLER einen besonders günstigen Einfluss auf die Morphologie des Niederschlages (leichte Filtrierbarkeit) ausübt.

SUMMARY

The authors have established, through their investigations with the electron microscope, that an addition of ammonium chloride at the time of the precipitation of $BaSO_4$, according to L. W. WINKLER, exerts an influence on the morphology of the precipitate (the latter then filtering easily).

Literatur S. 509.

RÉSUMÉ

Les auteurs ont établi, grâce à leurs recherches au microscope électronique, qu'une addition de chlorure d'ammonium lors de la précipitation de $BaSO_4$, selon L. W. WINKLER exerce une influence favorable sur la morphologie du précipité (celui-ci se filtrant alors facilement).

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Eingegangen den 19. Dezember 1953

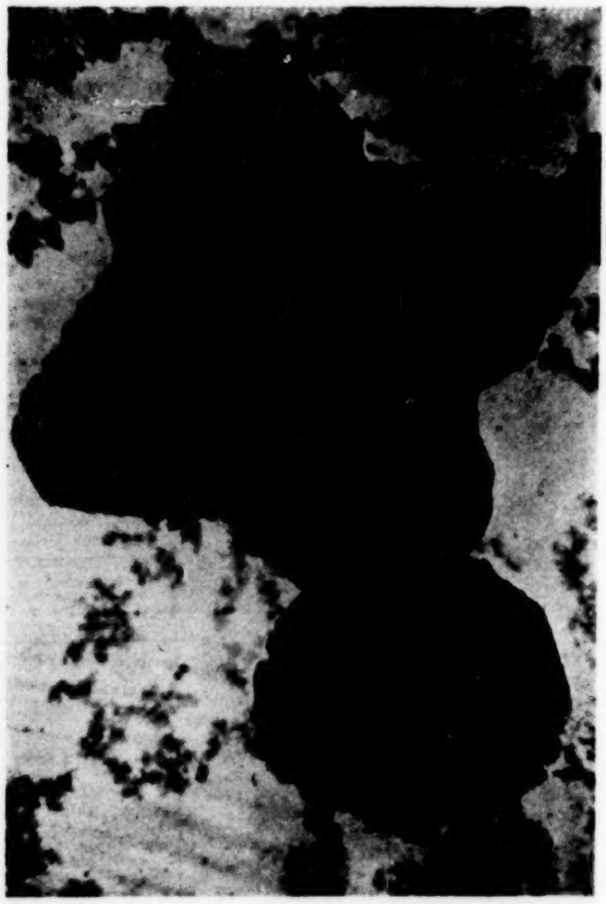

Fig. 1AE Vergr. 1 : 6300
$BaSO_4$ aus $2.5 \cdot 10^{-4} M$-er Lösung

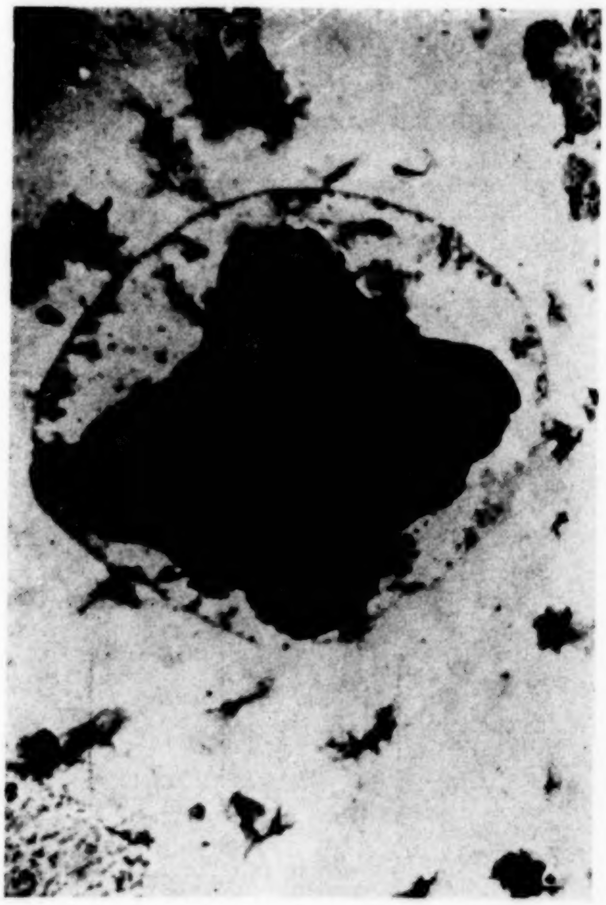

Fig. 2AE Vergr. 1 : 6000
$BaSO_4$ aus $2.5 \cdot 10^{-4} M$-er Lösung mit nachträglichem Zusatz von 2% NH_4Cl

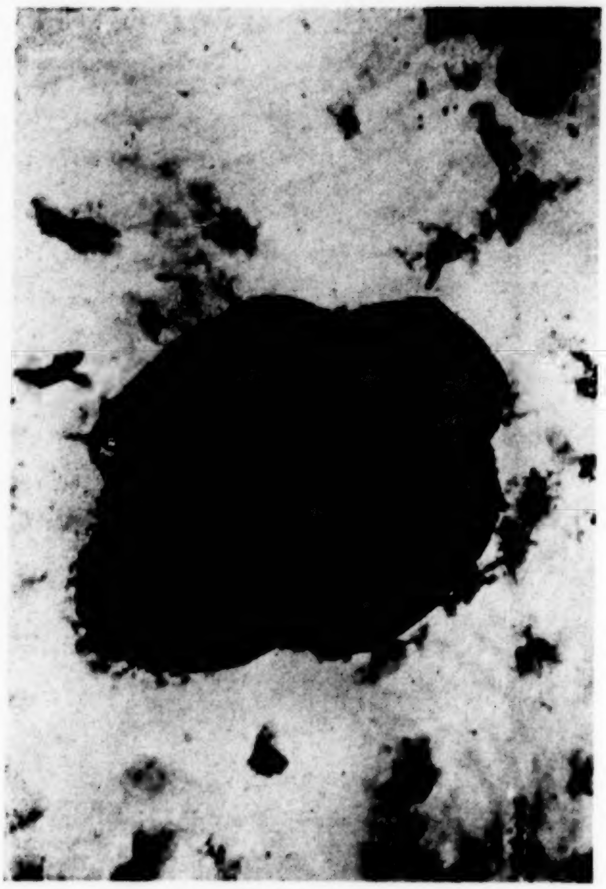

Fig. 3AE Vergr. 1 : 6000
$BaSO_4$ aus $2.5 \cdot 10^{-4}$ *M*-er Lösung mit nachträglichem Zusatz von 2% NH_4Cl

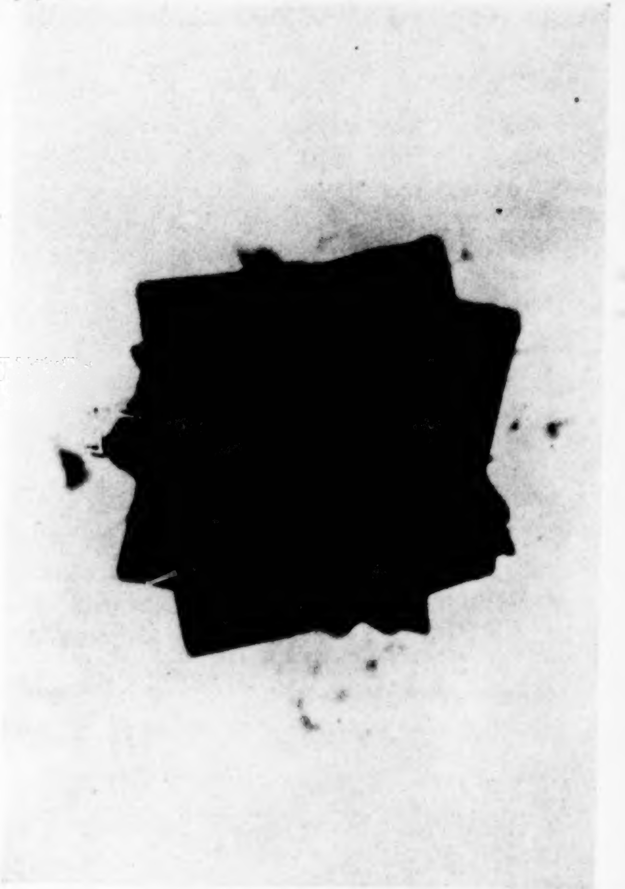

Fig. 4BE Vergr. 1 : 8400
$BaSO_4$ aus $2.5 \cdot 10^{-4}$ *M*-er Lösung. $5 \cdot 10^{-4}$ *M* Ba^{+2} im Überschuss

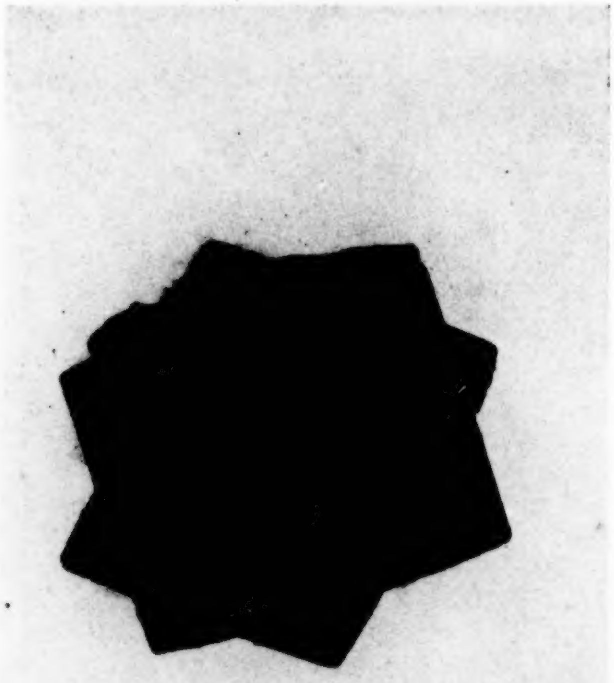

Fig. 5BE Vergr. 1 : 8400
$BaSO_4$ aus $2.5 \cdot 10^{-4}$ *M*-er Lösung. $5 \cdot 10^{-4}$ *M* Ba^{+2} im Überschuss

Fig. 6BE Vergr. 1 : 6000
$BaSO_4$ aus $2.5 \cdot 10^{-4}$ *M*-er Lösung. $7.5 \cdot 10^{-4}$ *M* Ba^{+2} im Überschuss

Fig. 7BE Vergr. 1 : 8250
BaSO$_4$ aus $2.5 \cdot 10^{-4} M$-er Lösung. $7.5 \cdot 10^{-4} M$ SO$_4^{-2}$ im Überschuss

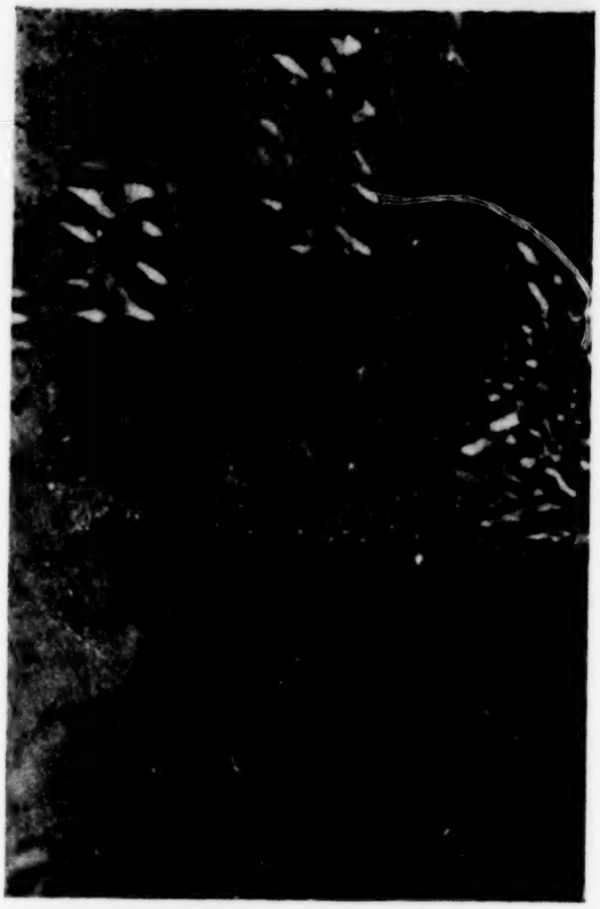

Fig. 8AL Vergr. 1 : 780
BaSO$_4$ aus $10^{-2} M$-er H$_2$SO$_4$ mit Ba^{+2}-Überschuss gefällt

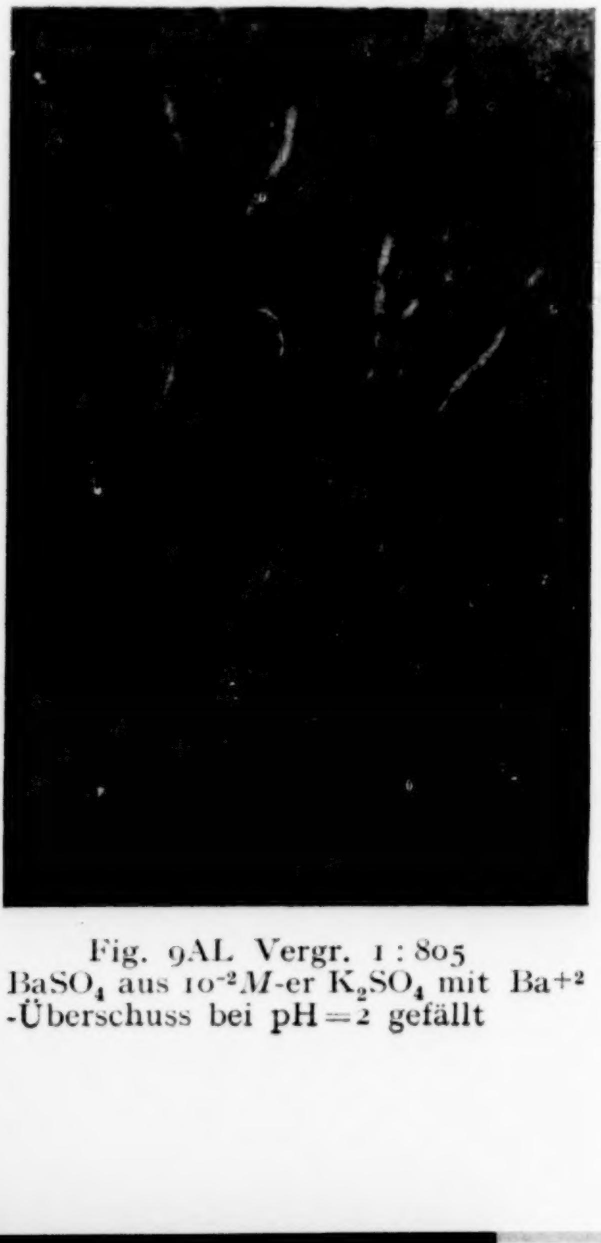

Fig. 9AL Vergr. 1 : 805
BaSO$_4$ aus $10^{-2} M$-er K$_2$SO$_4$ mit Ba^{+2} -Überschuss bei pH = 2 gefällt

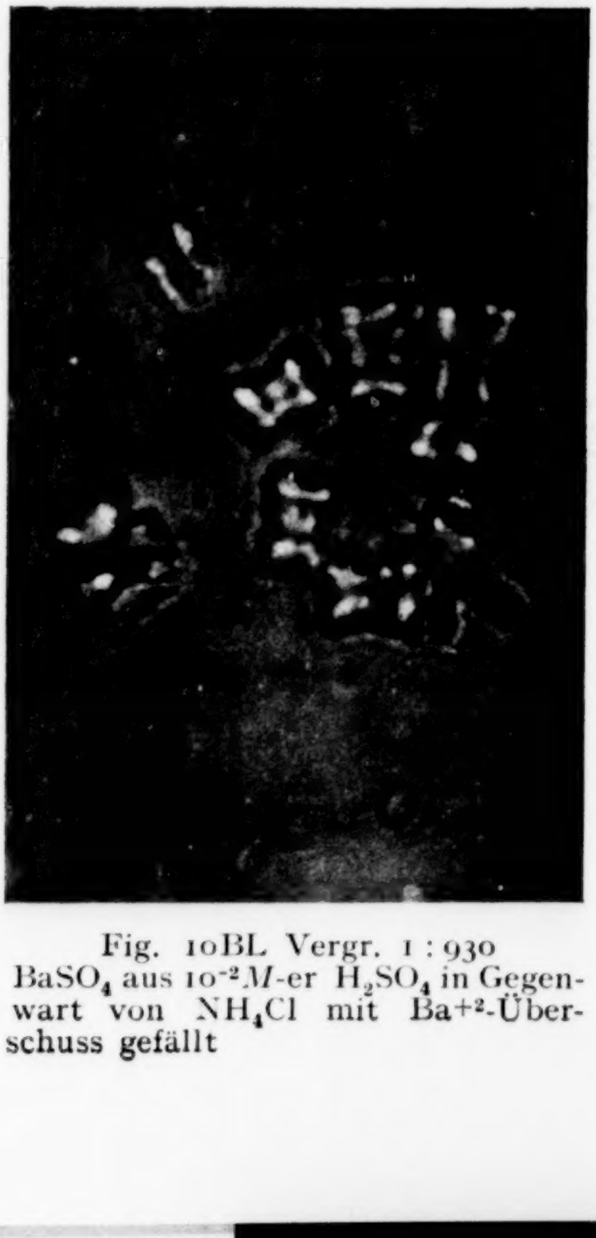

Fig. 10BL Vergr. 1 : 930
BaSO$_4$ aus $10^{-2} M$-er H$_2$SO$_4$ in Gegenwart von NH$_4$Cl mit Ba^{+2}-Überschuss gefällt

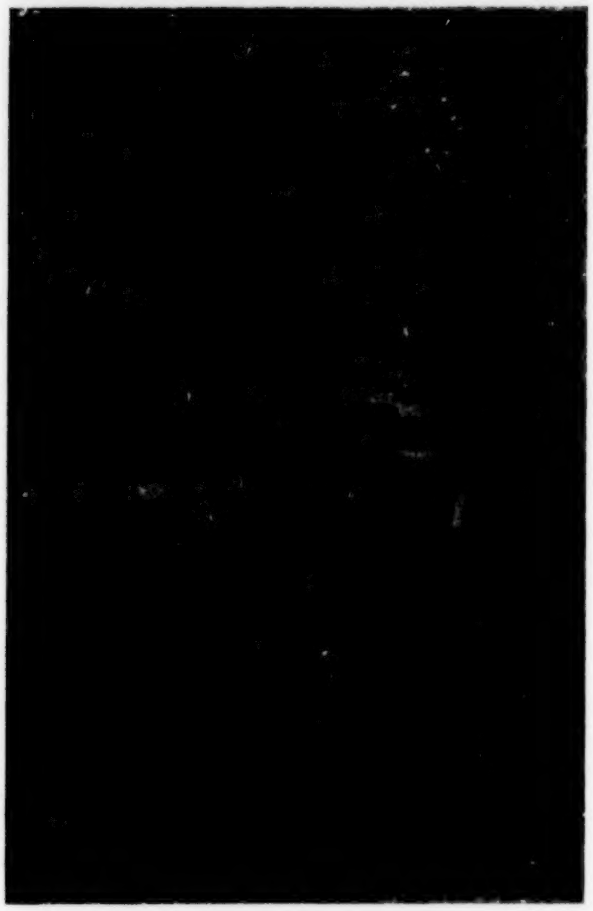

Fig. 11BL Vergr. 1 : 760
BaSO$_4$ aus $10^{-2}M$-er K_2SO_4 in Gegenwart von NH_4Cl mit Ba^{+2}-Überschuss bei pH = 2 gefällt.

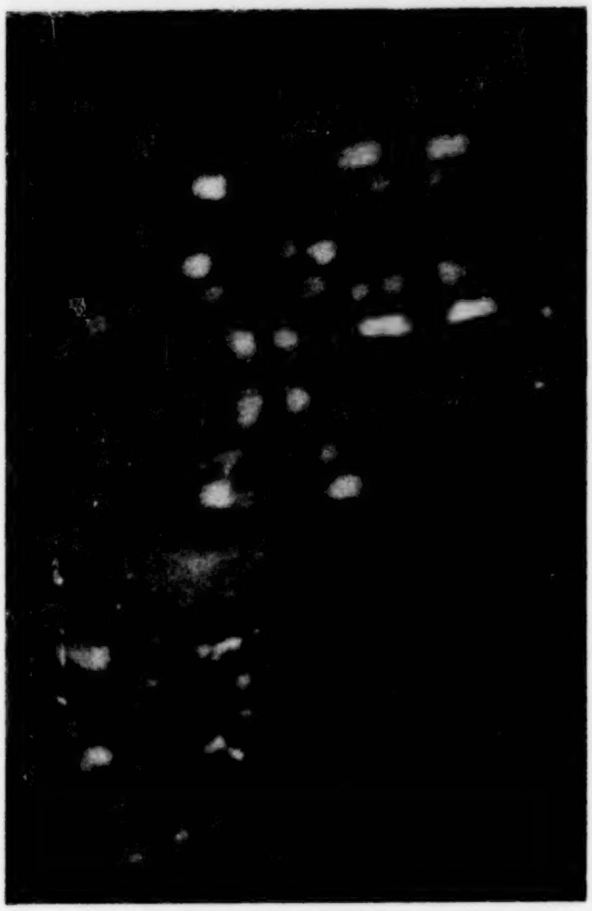

Fig. 12BL Vergr. 1 : 865
BaSO$_4$ aus $10^{-2}M$-er K_2SO_4 in Gegenwart von NH_4Cl bei pH = 2 gefällt

Fig. 13BL Vergr. 1 : 800
BaSO$_4$ aus $10^{-2}M$-er K_2SO_4 in Gegenwart von NH_4Cl „neutral" gefällt

ANALYSIS OF URANIUM-ZINC ALLOYS*

by

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Contribution No. 286 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa (U.S.A.)

INTRODUCTION

A method was needed for analyzing alloys of zinc and uranium containing up to 20% uranium. The following method is rapid, quantitative, and requires no separation of either component. The uranium is determined by passing a solution of the alloy through a lead reductor and then titrating with ceric sulfate[2]. The zinc is determined by titrating with Versene using ammonium purpurate as the indicator. The uranium does not interfere in the Versene titration if it is first complexed with carbonate.

REAGENTS

Versene

A 0.05*M* solution, prepared from the disodium salt of ethylenediaminetetraacetic acid. This solution was standardized against standard zinc chloride by the procedure given below for the analysis of zinc.

Zinc chloride

A 0.05*M* solution, prepared by dissolving 3.3 grams of pure zinc (weighed exactly) in 20 ml HCl and diluting to one liter.

Ammonium purpurate (Murexide)

1% aqueous solution, freshly prepared.

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* Work was performed in the Ames Laboratory of the Atomic Energy Commission.

PROCEDURE

Dissolve about 0.4 g of the sample in 10 ml HCl and add 30% H_2O_2 if necessary to effect solution. Dilute to 200 ml in a volumetric flask. Use this prepared solution for the following analyses.

Zinc

Dilute a 5.00 ml aliquot of the prepared solution to 70 ml. Pipette in exactly 10.00 ml of 0.05*M* Versene. Add solid sodium bicarbonate until the solution clears (about 2-3 grams) and adjust the pH to 8-8.5 with 1 to 9 HCl or 10% NaOH. Back titrate with standard 0.05*M* zinc chloride using 5-10 drops of 1% ammonium purpurate as the indicator. Subtract an indicator blank of 0.02 ml of zinc. The pH may have to be readjusted just before the end-point. The color change is magenta to orange.

Uranium

Pipette an aliquot of the prepared solution containing about 25 mg of uranium into a 250 ml beaker. Dilute to 80 ml with 3*N* HCl. Pass this solution through a lead reductor into a 1*N* solution of ferric alum. Titrate with 0.01*N* ceric sulfate using ferroin indicator.

DISCUSSION

Uranium precipitates as the hydroxide in the pH range used in the titration of the zinc and interferes with the end-point. The addition of carbonate keeps the uranium in solution by forming a soluble complex.

Normally Eriochrome Black T is used as the indicator in the titration of zinc [1,3,4,6,]; however, the carbonate is not sufficient to keep the uranium-indicator complex from forming. Ammonium purpurate has been suggested as a useful indicator for Versene titrations[5]. This indicator forms a weak complex with zinc and none with uranium when carbonate is present; therefore, it was used as the indicator in this titration. Ammonium purpurate solutions decompose on standing and must be prepared fresh each day.

The zinc-indicator complex is yellow colored. Because of the large concentration of indicator (5-10 drops of 1% solution) the titration must be carried only to the first noticeable change from magenta to orange. This avoids a large indicator error.

The end-point is sharper when there is less than 20% uranium present. To improve the end-point the pH should be adjusted to 8.0-8.5 just before the end-point is reached. When ammonium hydroxide was used to adjust the pH, no end-point was observed in the titration. Apparently the zinc-ammonia complex is stronger than the zinc-indicator complex; therefore, sodium hydroxide should be used to adjust the pH.

Several synthetic solutions of uranium and zinc were prepared and analyzed for zinc by the above procedure. The results are given in Table I.

Several samples were analyzed on a routine basis. Results are shown in Table II. The low results in the first two samples, which were metal turnings, indicate possible surface oxidation. The other samples were massive and were cleaned with HNO_3 and HF.

TABLE I

DETERMINATION OF ZINC IN KNOWN ZINC-URANIUM SOLUTIONS

% Zinc added	% Uranium added	% Zinc
80.0%	20.0%	80.2%
50.0%	50.0%	50.2%
20.0%	80.0%	20.1%

TABLE II

ROUTINE ANALYSES OF URANIUM-ZINC ALLOYS

Sample No.	% Zinc	% Uranium	Total Zn + U
OTE 1-5-1-3	80.20%	15.37%	95.7%
	80.43	15.34	96.7
OTE 1-5-2-3	79.80	16.87	96.7
	79.69	17.02	
OTE 1-10-1	93.37	6.96	100.0
	92.78	6.96	
12-1-1	99.98	0.04	100.0
	99.98	0.03	
12-1-2	100.04	0.33	100.4
	100.19	0.33	
12-1-4	94.50	5.02	99.7
	94.88	5.01	
12-1-5	86.88	14.21	101.1
	86.88	14.22	
12-1-6	85.88	14.41	100.4
	86.03	— —	
PW-1-4	85.29	15.19	100.5
	85.41	15.17	
PW-1-2	97.33	3.07	100.4
	97.33	3.08	

SUMMARY

Zinc can be determined in zinc-uranium alloys by titration with Versene (ethylenediaminetetra-acetic acid), using Murexide as the indicator. Carbonate is added before the titration to mask the uranium.

References p. 516.

RÉSUMÉ

Il est possible de doser le zinc dans les alliages zinc-uranium par titration avec l'acide éthylènediaminotétracétique, en employant la murexide comme indicateur. On ajoute du carbonate avant la titration pour masquer l'uranium.

ZUSAMMENFASSUNG

Zink kann in Zink-Uran Legierungen mit Versene (Äthylendiamintetraessigsäure) durch Titration bestimmt werden, indem Murexid als Indikator benützt wird. Um das Uran zu maskieren, werden Karbonate vor der Titration zugefügt.

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A DIRECT TITRIMETRIC DETERMINATION OF BARIUM WITH ETHYLENEDIAMINETETRA-ACETATE

by

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The titration of calcium and magnesium ions, also the total hardness, with ethylenediaminetetra-acetate and eriochrome black T as an internal indicator is accurate. We have now tried to determine barium ions in the same way.

BIEDERMANN AND SCHWARZENBACH[1], however, concluded from their investigations on the complexone formation of ethylenediaminetetra-acetic acid: "Hingegen ist Ba auch nach Zusatz von Mg nicht mit F 241 (= eriochrome black T) titrierbar, weil hier auch in der ammoniakalischen Lösung das Mg dem Ba vorgezogen wird vom Ion Y^{-4} (= ethylenediaminetetra-acetate)".

MUNGER, NIPPLER AND INGOLS[2] titrated the barium ions in the same way as the total hardness. The end-point was indistinct and very slow. After this bad end-point was reached, they added a fixed amount of magnesium chloride to the solution and titrated to a very sharp and real end-point, similar to that of the hardness titration.

We tried to avoid the addition of a fixed amount of magnesium chloride.

In our first tests we titrated a known amount of barium chloride solution, following the same method as described for the titration of the total hardness[3] using 2 ml of the ammonia-ammonium chloride buffer which contained 1 g per litre of the magnesium salt of ethylenediaminetetra-acetic acid (B. Siegfried, Zofingen Switzerland). We found that the end-point of the titration was not very distinct but addition of more buffer solution gave a better end-point.

As the buffer solution contains magnesium complexone and the change in the colour of the indicator is the sharpest with magnesium, the influence of the amount of magnesium complexone in the buffer solution was investigated.

From Table I it follows that, using 2 ml of the buffer solution which contains 10 g or more magnesium complexone per litre, the end-point is a sharp one, the indicator changing rapidly from red to a pure blue colour.

When we used a barium chloride solution, which was acidified by 1 ml 2*N* HCl, the pH after titration was 9.90. Therefore we added the same amount of

TABLE I

INFLUENCE OF THE AMOUNT OF MAGNESIUM ETHYLENEDIAMINETETRA-ACETIC ACID ON THE CHANGE IN COLOUR AT THE END-POINT

Amount of magnesium complexone per litre of buffer solution	End-point
50 g	good
10 g	good
1 g	bad, indistinct

25% NH_4OH to the buffer solution and used 4 ml of this. The pH after titration was now 10.02 and the change in colour at the end-point was sharp.

The titrating procedure is as follows:

Standard ethylenediaminetetra-acetic acid

6.64 grams of disodium dihydrogen ethylenediaminetetra-acetic acid (I.C.I.) are dissolved in sufficient water to make 1 litre of solution. This solution was standardized against a standard calcium solution[3].

Ammonia-ammonium chloride buffer solution

10 grams of dipotassium magnesium ethylenediaminetetra-acetic acid (B. Siegfried, Zofingen Switzerland) are dissolved in 200 ml of water and added to a solution of 70 g ammonium chloride in 1800 ml of ammonia (25%).

TABLE II

ANALYSES OF KNOWN AMOUNTS OF BARIUM CHLORIDE BY TITRATING WITH ETHYLENEDIAMINETETRA-ACETATE SOLUTION

Amount of barium chloride added mg	found mg	difference in mg	in %
2.75	2.80	+ 0.05	+ 2.0
5.50	5.55	+ 0.05	+ 1.0
13.74	13.91	+ 0.17	+ 1.4
27.48	27.75	+ 0.27	+ 1.1
41.22	41.49	+ 0.27	+ 0.7
54.95	55.42	+ 0.47	+ 0.9
82.43	83.03	+ 0.60	+ 0.8
109.90	110.45	+ 0.55	+ 0.5

Indicator solution

0.5 g of eriochrome black T (Solochrome Black W.D.F.A.) (I.C.I.) and 4.5 g of hydroxylamine hydrochloric acid are dissolved in 100 ml of alcohol (96%).

Titration:

To 100 ml of barium chloride solution, which is acidified by 1 ml 2*N* HCl, 4 ml of the ammonia-ammonium chloride buffer solution are added and 7 drops of the eriochrome black indicator solution.

The solution is titrated at once with the standard ethylenediaminetetra-acetate solution to a pure blue end-point.

In Table II the results of the titration of known amounts of barium chloride are given.

From these figures we see that the agreement is reasonably good, although the amount found is always a little higher than the given amount.

As mentioned, the titer of the ethylenediaminetetra-acetate solution is standardized with pure calcium carbonate. If it were standardized with barium chloride solution, the differences between the amounts of barium chloride taken and found would be much smaller.

I am very much indebted to Mr. P. C. VAN VLIET, for the analyses which he has carried out.

SUMMARY

A method is given for the titrimetric determination of barium ions with ethylenediaminetetra-acetate, using a modified buffer solution; it is similar to the total hardness titration.

RÉSUMÉ

Une méthode est proposée pour le dosage volumétrique du baryum au moyen de l'anion éthylènediaminotétracétique, la solution tampon étant modifiée; cette méthode est analogue à celle de la détermination de la dureté totale.

ZUSAMMENFASSUNG

Es wird eine Methode zur titrimetrischen Bestimmung von Bariumionen mit Äthylendiamintetraacetat unter Benützung einer abgeänderten Pufferlösung gegeben; sie ist ähnlich wie die Titration der Gesamthärte.

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ANALYSE ORGANIQUE FONCTIONNELLE
I. ANALYSE THERMOGRAVIMÉTRIQUE DES DINITRO-2,4 PHÉNYLHYDRAZONES

par

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INTRODUCTION

On sait que *l'Union internationale de chimie pure et appliquée,* au cours de sa session de Stockholm en juillet 1953, a créé, dans la section de Chimie analytique, une sous-commission d'Analyse organique fonctionnelle comprenant MM. CLÉMENT DUVAL (Paris), président et STIG VEIBEL (Copenhague), secrétaire et que le premier objectif de cette nouvelle sous-commission sera de rassembler et de critiquer les modes d'analyse qualitative et quantitative du groupement carbonyle des aldéhydes et des cétones.

Le problème sera envisagé sous un aspect très large car nous retiendrons les modes d'analyse spectrographique relatifs à l'infrarouge et à l'effet Raman, la formation des réactions colorées, de fluorescence, de précipitation, les modes de dosage gravimétrique, titrimétrique, gazométrique, spectrocolorimétrique, polarographique, les électrotitrages divers et, finalement, les dosages biologiques.

C'est pourquoi, nous présentons aujourd'hui le premier mémoire d'une série concernant le dosage pondéral de quelques aldéhydes et cétones à l'aide de la dinitro-2,4 phénylhydrazine comme réactif.

MODE OPÉRATOIRE

L'aldéhyde ou la cétone à doser, préalablement purifié est dissous dans un excès d'alcool éthylique à chaud et maintenu à reflux pendant un temps variant de 5 à 15 minutes avec un excès (environ 1/10 du poids calculé) de dinitro-2,4 phénylhydrazine purifiée, également dissoute dans l'alcool. On laisse déposer le précipité jaune ou rouge apparu par refroidissement, pendant une demi-heure environ. On le décante, le lave par centrifugation plusieurs fois avec l'alcool pour éliminer l'excès de réactif.

Les courbes de thermolyse de tous les précipités obtenus ont été enregistrées avec la *thermobalance à plume* déjà décrite (CLÉMENT DUVAL — *Inorganic Thermo-*

gravimetric Analysis, Elsevier, Amsterdam, 1952, page 28). Le chauffage a toujours été effectué linéairement en fonction du temps, à raison de 150° par heure. Les poids de précipités utilisés ont varié de 80 à 200 mg.

Nous avons opéré avec 14 aldéhydes et 19 cétones pris dans diverses séries et qui sont rangés dans le tableau suivant avec la température correspondante de fusion de la dinitro-2,4 phénylhydrazone que nous avons mesurée sur le bloc.

Aldéhydes	
Formaldéhyde	166°
Acétaldéhyde	168°
Isovalérylaldéhyde	123°
Heptaldéhyde	107°
Benzaldéhyde	237°
p-Chlorobenzaldéhyde	269°
m-Nitrobenzaldéhyde	292°
p-Hydroxybenzaldéhyde	280°
Anisaldéhyde	253°
Cinnamaldéhyde	257°
o-Vanillal (hydroxy-2 méthoxy-3 benzaldéhyde)	240°
Vanillal (hydroxy-4 méthoxy-3 benzaldéhyde)	271°
Pipéronal	265°
Thénaldéhyde-2	233°

Cétones	
Acétone	125°
Méthyléthylcétone	111°
Acétophénone	249°
p-Chloroacétophénone	235°
p-Terbutylacétophénone	218°
Dichloro-3,4 acétophénone	258°
Cyclopentanone	146°
Cyclohexanone	162°
p-Hydroxypropiophénone	255°
Méthoxy-4 iodo-3 propiophénone	272°
Méthoxy-4 fluoro-3 propiophénone	256°
Méthyl-2 fluoro-4 propiophénone	128°
Méthyl-2 fluoro-4 butyrophénone	193°
p-Ethylbenzophénone	174°
p-Propylbenzophénone	167°
p-Butylbenzophénone	159°
Méthoxy-4 iodo-3 benzophénone	216°
(Fluoro-2 méthyl-5) phényl-benzylcétone	178°
(Fluoro-4 méthyl-2) phényl-benzylcétone	189°

INTERPRÉTATION

Les dinitro-2,4 phénylhydrazones relatives aux 33 corps ci-dessus ont été chauffées jusqu'au point de fusion indiqué ou à quelques degrés au-dessus. D'une manière générale, tous ces corps sont remarquablement stables jusqu'au point de fusion, sauf le dérivé de la méthoxy-4 iodo-3 propiophénone qui fond à 272° mais qui, dès 270° accuse déjà une perte de poids notable.

Les courbes relatives à la *p*-méthoxybenzophénone et à la *p*-éthylbenzophénone descendent très lentement jusqu'au point de fusion. Le dérivé de la *p*-butylbenzophénone se décompose en atteignant le sien.

Dans la plupart des cas, nous avons donc obtenu des *droites* parfaitement horizontales depuis la température ordinaire; parfois, comme dans le cas de l'anisaldéhyde, le précipité retient sans doute par adsorption, malgré plusieurs lavages, un peu de réactif précipitant qui disparait progressivement par chauffage jusque vers 100°; après quoi, on obtient un palier parfaitement horizontal jusqu'au point de fusion.

CONCLUSION

On peut dire qu'à part deux exceptions peu importantes, les 14 aldéhydes et les 19 cétones examinés dans ce travail peuvent être pesés après séchage de leur dinitro-2,4 phénylhydrazone, soit, après maintien à froid dans le dessiccateur à vide, soit après séjour pendant une dizaine de minutes à une température comprise entre 20° et le point de fusion que nous rappelons dans les deux tableaux précédents.

Nous ne jugeons pas utile de reproduire les droites horizontales obtenues.

Nous remercions Mlle COLETTE WADIER qui nous a beaucoup aidé dans la préparation de ces enregistrements.

RÉSUMÉ

Les auteurs ont tracé et étudié les courbes de thermolyse des dinitro-2,4 phénylhydrazones de 14 aldéhydes et de 19 cétones en vue de leur usage en analyse pondérale.

SUMMARY

The authors have traced and studied the thermolytic curves of 2,4-dinitrophenylhydrazones of 14 aldehydes and of 19 ketones with regard to their use in gravimetric analysis.

ZUSAMMENFASSUNG

Die Autoren haben die Kurven der Thermolyse der 2,4-Dinitro-phenylhydrazone von 14 Aldehyden und 19 Ketonen hinsichtlich ihrer Verwendung bei der Gewichtsanalyse aufgezeichnet und untersucht.

Reçu le 15 décembre 1953

THE ANALYSIS OF COMBUSTION PRODUCTS

II. THE ESTIMATION OF TRACES OF METHANOL IN THE PRESENCE OF FORMALDEHYDE

by

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In studies on the oxidation of the lower hydrocarbons, a problem which is often encountered is the analysis of traces of methanol in the condensed products of reaction, which may contain large amounts of formaldehyde as well as peroxides. Of the methods available for the detection and estimation of methanol, the suitable ones for dealing with very small quantities include the xanthate test, the formation of derivatives such as *p*-bromobenzoate, and oxidation to formaldehyde which can be accurately estimated with the chromotropic acid reagent. The xanthate colorimetric test, which can detect 10^{-4} g of alcohol, was found to fail in the presence of formaldehyde. The methods involving the formation of derivatives, besides being cumbersome, are hardly suitable for the detection of very small quantities of methanol, as the yields of the derivatives are often low. DILLER[1] found that in the case of the *p*-bromobenzoyl derivative of methanol the yield was only 40—45% even when 25 times excess of *p*-bromobenzoyl chloride was used. The third type of method, the estimation of formaldehyde resulting from the oxidation of methanol, is the most sensitive one for the analysis of methanol, but is rendered inaccurate by the need to measure a small difference between two large quantities. A satisfactory method for the separation of methanol from formaldehyde is clearly required.

DILLER tried to separate methanol by distillation, either after destroying the formaldehyde with alkaline silver solution according to the method of JANSCH[2], or after condensing the formaldehyde with sodium sulphanilate. However, he found that along with methanol small amounts of formaldehyde were always present in the distillate. The use of 'dimedone' for the precipitation of formaldehyde according to the method of YOE AND REID[3] was considered. Again, this method is unsatisfactory as it requires at least 12 hours for the precipitation of formaldehyde, which, moreover, is never complete.

The method described in this note solves the problem simply, by separating methanol from a large excess of both formaldehyde and hydrogen peroxide by paper chromatography, followed by the oxidation of the methanol to formaldehyde which is estimated colorimetrically with chromotropic acid.

EXPERIMENTAL

The solution under test is treated with sodium bisulphite. A drop of the solution is then placed on a strip of Whatman No. 1 filter paper and the chromatogram developed with ether in the usual manner. This results in the movement of the methanol with the solvent front, while the concentration of formaldehyde and hydrogen peroxide remains a maximum at the point of application of the solution. The chromatographic separation between methanol and formaldehyde can be further improved by using a filter paper which has been previously treated with sodium bisulphite.

For detecting the presence of methanol on the chromatogram, the filter paper is cut into a number of successive portions, and each is extracted with 1—2

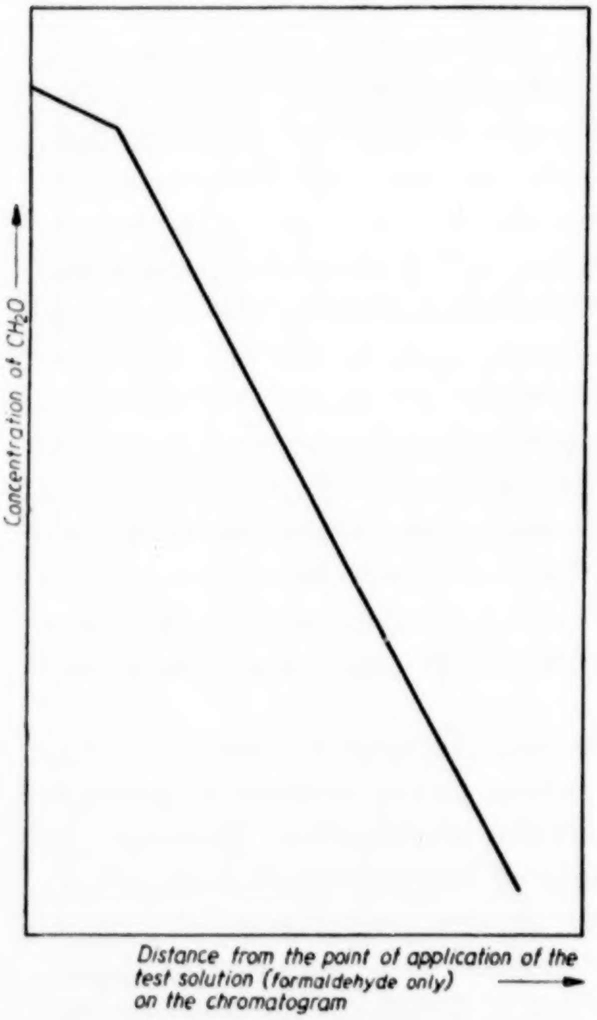

Fig. 1

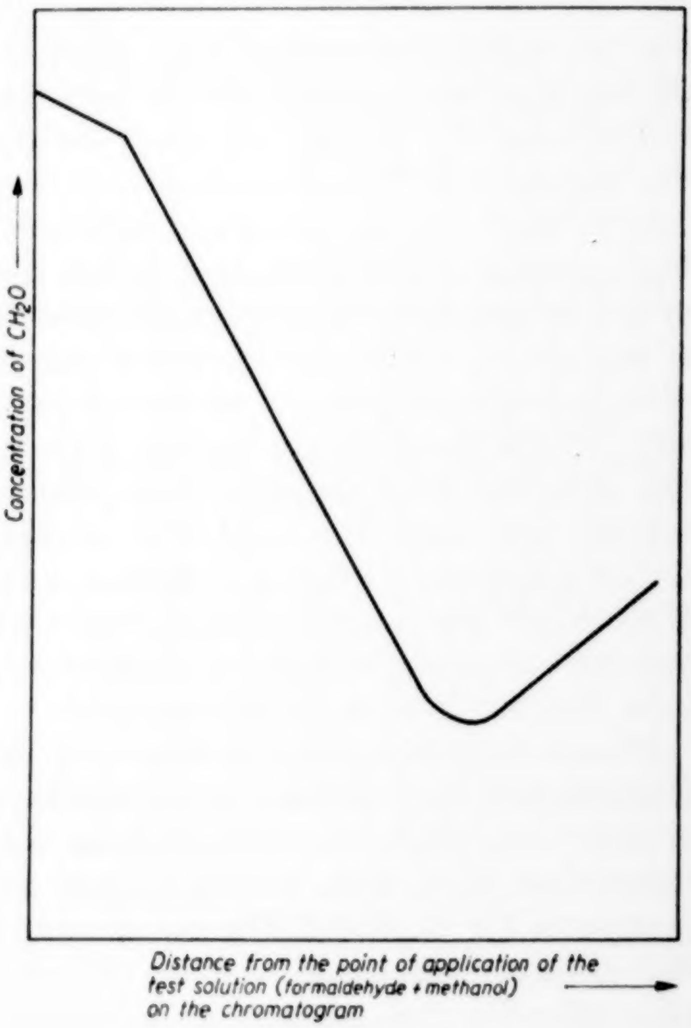

Fig. 2

References p. 525.

ml of water. The solutions are treated, according to the method of Boos[4], with a few drops of acidified dilute solution of potassium permanganate for ten minutes. The excess potassium permanganate is destroyed by adding dropwise a solution of sodium bisulphite. To the clarified solution, 1 ml of 1% chromotropic acid solution is added followed by the addition of 6 ml of concentrated sulphuric acid. The solutions are then heated in a water bath for half an hour, cooled and made up to a known volume, usually 10 ml. The intensity of the violet red colour formed is then estimated on a spectrophotometer at 5700 A[5].

When there is no methanol present in the mixture, the intensity of colour due to formaldehyde is found to be a maximum in the portion of the filter paper nearest the point of application of the test solution, and then to fall off sharply (Fig. 1). In the presence of methanol, however, the intensity of the colour is found to rise again at the other end of the chromatogram as shown in Fig. 2.

SUMMARY

In the analysis of combustion products, the estimation of traces of methanol can be rendered difficult by the presence of excess formaldehyde. A method is described for separating the formaldehyde from methanol by treating the solution with sodium bisulphite, and then carrying out a chromatographic separation on filter paper. Ether carries the methanol to the end of the strip, leaving behind formaldehyde and hydrogen peroxide. The paper is cut into pieces, which are separately extracted with water, and the solution oxidised. The formaldehyde so formed is estimated in the usual way with chromotropic acid.

RÉSUMÉ

Lors de l'analyse des produits de combustion, le dosage des traces de méthanol peut être rendu difficile par la présence de formaldéhyde en excès. Une méthode est décrite pour la séparation formaldéhyde-méthanol: on traite la solution par le bisulfite de sodium puis on effectue une séparation chromatographique sur papier filtre. L'éther entraîne le méthanol tandis que le formaldéhyde et le peroxyde d'hydrogène restent en arrière. Pour déceler le méthanol, le papier est coupé en plusieurs morceaux. Ceux-ci sont traités séparément par l'eau, puis par l'oxydant. Le formaldéhyde ainsi formé est dosé par le procédé à l'acide chromotropique.

ZUSAMMENFASSUNG

Bei der Analyse von Verbrennungsprodukten kann die Bestimmung von Spuren Methanol durch die Anwesenheit von Formaldehyd erschwert werden. Es wird eine Methode zur Abtrennung des Formaldehyds vom Methanol durch Behandlung der Lösung mit Natriumbisulfit und Ausführung einer chromatographischen Trennung auf Filterpapier beschrieben. Äther bringt Methanol zum Streifenende und lässt Formaldehyd und Wasserstoffsuperoxyd zurück. Das Papier wird in Stücke geschnitten, die getrennt mit Wasser extrahiert werden; diese Lösungen werden dann oxydiert. Der so gebildete Formaldehyd wird in der üblichen Weise mit Chromotropsäure bestimmt.

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ÉTUDE SUR LE DOSAGE COLORIMÉTRIQUE DE L'ALUMINIUM DANS LES ACIERS

par

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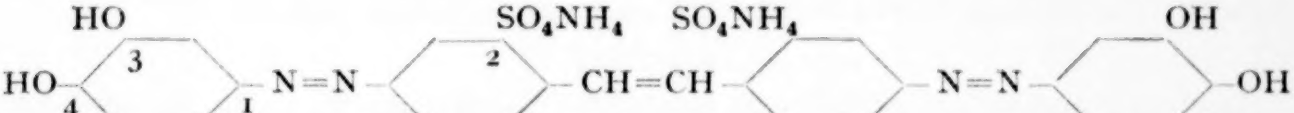
OBJET DE L'ÉTUDE

(1) KOUZNETSOV, KARANOVITCH ET DRAPKINA[1] ont fait connaître, pour le dosage colorimétrique de l'aluminium, un réactif nouveau, le sel diammonique de l'acide stilbène -4-4′ [(azo) 3,4 dioxybenzol] 2,2′-disulfonique (ou stilbazo):



Les auteurs précités étudient ce colorant comme réactif de l'aluminium, et aboutissent à un mode opératoire valable pour les minerais de fer et pour diverses autres substances (cendres de végétaux, de caoutchouc, de papier, etc.).

(2) Selon le mémoire original, ce réactif, sensible à des concentrations de 10 γ/l d'Al, est applicable en présence de petites quantités de fer (0.5 à 1 mg Fe-II) et de titane (0.1 mg).

Or, les réactions colorées des deux réactifs classiques de l'aluminium, l'aurinetricarboxylate d'ammonium et l'éryochromcyanine, sont perturbées par de très petites quantités de fer, même après séparation électrolytique de celui-ci sur cathode de mercure, d'où la nécessité, dans l'analyse des produits technologiques, spécialement des aciers, de séparations supplémentaires rigoureuses. Le titane, qui réagit également avec ces réactifs et n'est au reste pas éliminé sur cathode de mercure, doit être séparé spécialement.

L'affirmation des auteurs russes que la réaction de l'aluminium au stilbazo ne serait pas influencée par des quantités de fer et de titane qui certainement perturberaient celles à l'aluminon et à l'éryochromcyanine, revient à attribuer à ce réactif un réel avantage sur les deux derniers. En outre la grande sensibilité du stilbazo à l'aluminium permettrait de doser celui-ci directement dans les aciers alliés à l'aluminium, la faible prise d'essai d'acier dès lors possible n'amenant qu'une quantité de fer suffisamment petite pour qu'elle soit compatible avec la tolérance du réactif vis-à-vis du fer.

(3) Le présent travail comporte donc l'étude du dosage de l'aluminium au moyen du stilbazo, en vue de la détermination de cet élément dans les aciers. La technique à laquelle on a abouti a été utilisée en vue du dosage de l'aluminium de calmage dans les aciers, au cours d'une étude antérieure*.

Incidemment, une technique pour le dosage de l'aluminium dans les zincs a été établie**.

PARTIE THÉORIQUE

(4) Parmi les nombreuses indications que comporte la publication originale, on relève en particulier les suivantes.

Le pH optimum du développement de la réaction colorée se situe vers pH 5.2 à 5.6 et est obtenu au moyen d'un tampon acéto-acétique. Le fer est réduit au stade Fe-II, et est complexé par l'acide ascorbique.

Le titane, si la quantité dans le milieu du dosage final dépasse la dose indiquée (0.1 mg), est éliminé au moyen de la 5.7-dibromo-8-oxyquinoléine. Le titrage colorimétrique final est fait dans un très petit volume, de l'ordre de 5 ml; un témoin, fait dans les conditions mêmes de l'essai réel, est titré au moyen d'une liqueur standard d'aluminium jusqu'à égalité de teinte de l'un et l'autre liquide, et la teneur en aluminium à doser déduite du volume de liqueur aluminique versé dans le témoin.

Enfin, la préparation, au reste aisée, du stilbazo, est décrite dans le mémoire original.

(5) Il a paru souhaitable d'éviter l'emploi de l'acide ascorbique et de la bromoxine, réactifs peu courants.

Le mode opératoire du dosage final, peu pratique, a semblé perfectible grâce à l'emploi du photomètre.

Les auteurs, enfin, n'envisagent pas le cas du dosage de l'aluminium dans les aciers.

C'est pourquoi l'étude de la méthode a été reprise totalement, en vue du but poursuivi dans le présent travail.

(6) Le réactif en cause comporte, dans sa constitution, deux groupements phénoliques et un groupement azoté sur le même noyau.

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* Circulaire d'Informations Techniques du C.D.S. (Février 1954).

** A paraître.

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Il convient de rappeler ici que dans des travaux antérieurs j'ai indiqué que des réactifs comportant ces groupements fonctionnels devraient être spécifiques de l'aluminium. Ces études, dont le but était d'obtenir un réactif organique de l'aluminium pour sa séparation et son dosage pondéral, n'avaient toutefois pas été couronnées du succès pratique escompté: le stilbazo vient leur apporter une confirmation de principe, bien que la solution pratique soit trouvée dans la voie colorimétrique.

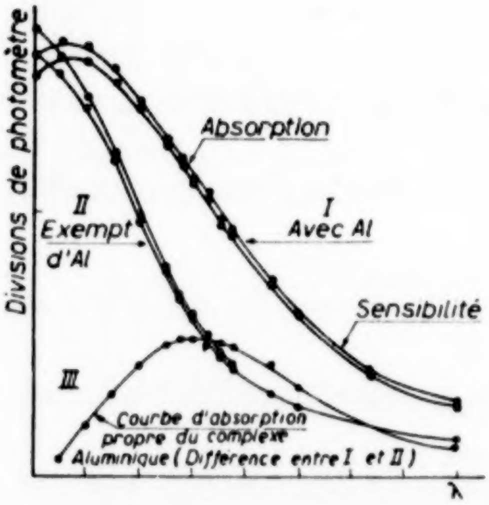
PARTIE EXPÉRIMENTALE

(7) *Réaction colorée au stilbazo en milieu acéto-acétique*

Le mode opératoire suivant est calqué sur celui des auteurs russes.

A des volumes variables (0; 1; 2 etc.... 10 ml) d'une liqueur d'aluminium (2.5 γ/ml Al) sont ajoutés: 10 ml de réactif stilbazo (1 g/l); 5 ml de solution d'acétate de sodium (250 g/l); 20 ml de tampon (30 ml de liqueur $M/5$ d'acide acétique et 170 ml de solution $M/5$ d'acétate de sodium; total 200 ml) et l'on complète à 100 ml en fioles jaugées.

Les courbes d'absorption, en fonction de la longueur d'onde, de l'essai témoin (exempt d'aluminium) et de l'un des termes de la gamme, indiquent pour l'optimum d'absorption λ = 5150 A, radiation pour laquelle la différence d'absorption entre le témoin et l'essai est maximum (Fig. 1).



La coloration propre du stilbazo impose que toutes les mesures soient faites en colorimétrie *différentielle:* réglage au zéro du photomètre à l'aide de l'essai témoin exempt d'aluminium, pour λ = 515 mμ; avec le photomètre Jean et Constant, opérer avec l'aide de la surcharge optique, la longueur de cuve étant choisie de manière que la densité optique soit 1 environ pour le témoin, et légèrement inférieure à 2 pour l'essai maximum de la gamme (dans l'exemple choisi, 25 γ Al).

La gamme ci-dessus se traduit par une droite: densité optique en fonction des quantités d'aluminium.

(8) D'une étude systématique, il résulte que la densité optique augmente avec le pH, pour une même quantité d'aluminium. L'optimum de sensibilité des dosages a été trouvé pour pH 5.5 à 5.6 et, dans toute cette étude, le pH des milieux de dosages photométriques a été contrôlé à l'électrode de verre.

(9) *Influence du fer*

La validité du dosage de l'aluminium par le stilbazo, et par voie photométrique,

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étant acquise, l'influence du fer a été envisagée. Une coloration brun noir se produit avec le fer à l'état ferrique. Il a donc été nécessaire de le réduire à l'état ferreux comme indiqué par les auteurs russes. L'acide ascorbique qu'emploient ceux-ci, soit pour réduire seulement le fer, soit peut-être aussi pour le complexer, a paru *à priori* d'un choix peu heureux en raison de sa rareté relative.

Il a été tout d'abord fait appel à *l'hydroxylamine*, réducteur d'emploi courant. Vérification est tout d'abord faite que l'hydroxylamine n'apporte aucune perturbation dans le dosage de l'aluminium.

Si dans une gamme, on introduit les quantités variables d'aluminium, 0.2 mg de fer (à l'état de sulfate ferrique), 20 ml de tampon acéto-acétique (30 ml d'acide acétique $M/5$ et 170 ml de solution d'acétate de sodium $M/5$), 5 ml de solution d'acétate de sodium (250 g/l), 10 ml de stilbazo (1 g/l) et de l'eau pour compléter à 100 ml, les essais sont tous fortement colorées en brun, par suite de l'action du ferferrique.

Si maintenant, dans une telle gamme, on ajoute, après le fer, 2 ml de solution de chlorhydrate d'hydroxylamine (100 g/l), la coloration brune due au fer se développe dans tous les termes, d'abord lentement, puis de manière plus accentuée avec le temps.

L'hydroxylamine est donc incapable de maintenir le fer à l'état ferreux, et d'inhiber sa réaction avec le stilbazo.

(10) On peut complexer de manière stable le fer à l'état ferreux au moyen de différents anions. Mais ceux-ci forment également des complexes avec l'aluminium: tel est le cas des citrates, tartrates, phosphates, pyro- et méta-phosphates*. Ces derniers réactifs employés soit seuls, soit en milieu acéto-acétique, avec ou sans introduction d'hydroxylamine, inhibent la réaction colorée du stilbazo avec l'aluminium. Même inhibition de cette réaction en présence des anions borique, phtalique, fluorhydrique, malonique et du trilon B. Les oxalates eux-mêmes, employés conjointement avec le tampon acéto-acétique, ou seuls, sous forme de tampon acide oxalique-oxalate d'ammonium, se comportent de la même façon.

(11) On a tenté de complexer le fer au moyen de différents réactifs, classiquement utilisés dans ce dessein.

Avec *l'acide thiomalique* (0.5 g pour 0.5 mg de fer), le fer, qu'il soit à l'état ferreux ou ferrique, commence à donner une coloration bleue à pH 4, et au dessus. Si donc ce réactif peut être employé pour complexer le fer en milieu d'acidité supérieure à pH 4, il ne peut plus l'être pour des acidités moindres; or à pH 4 la réaction du stilbazo avec l'aluminium n'a plus lieu: il y a donc incompatibilité dans l'emploi de l'un et l'autre de ces réactifs.

L'acide thioglycolique donne avec le fer à pH 5.5 la coloration bleue, qui tend à disparaître lorsque la proportion de réactif vis-à-vis du fer augmente (0.5 ml de réactif pur pour 1 mg de fer). Toutefois la coloration de l'aluminium avec le stilbazo est alors très instable.

(12) Seul donc l'acide ascorbique paraît à retenir en vue du but poursuivi. Il est capable, en milieu acéto-acétique et à pH 5.5, d'inhiber jusqu'à 2 mg de fer vis-à-vis de la réaction au stilbazo.

A 12.5 γ d'aluminium, dans différents essais, on ajoute des quantités variables de fer (sous forme de sulfate ferrique), 20 ml de solution d'acide ascorbique (50 g/l), le tampon acéto-acétique convenable, 10 ml de réactif stilbazo (0.5 g/l) et complète à 100 ml (pH final 5.5 environ).

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* Constantes de stabilité pK de quelques-uns de ces complexes:
phosphate Al: 6 ; phosphate Fe: 9.4
fluorures Al: 9.4 et 27; fluorures Fe: 2.2
oxalate Al: 3.3 et 13; oxalate Fe: 6 et 10.

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Les mesures photométriques, par rapport à un témoin exempt d'aluminium et de fer, sont consignées dans le Tableau I.

Donc 2 mg de fer dans le milieu de la réaction sont sans influence notable sur le dosage de l'aluminium, et il peut être admis 4 mg de fer, si la gamme d'étalonnage comportant des doses variables d'aluminium contient une quantité de fer de même ordre de grandeur.

De telles gammes, à aluminium variable (jusqu'à 50 γ Al) et à fer constant (1 mg), donnent des droites identiques à celles que l'on obtient, sans acide ascorbique ni fer, pour des pH finaux identiques.

C'est à partir de ces résultats qu'a pu être fait le travail concernant le dosage de l'aluminium dans les zinc*.

TABLEAU I

RÉSULTATS DE MESURES PHOTOMÉTRIQUES

mg Fe	0	0.1	0.2	0.5	1	2	3	4	5
mesure photométrique	31	31	31	31	31.5	31.5	32	32.5	34.5

(13) *Influence du titane*

Cet élément donne, dans le milieu de la réaction au stilbazo, une coloration rouge-violet à brun selon la quantité de titane en présence, ou selon le pH final.

L'acide succinique, déjà utilisé avec succès dans un cas analogue pour inhiber l'influence du titane[2], l'acide malonique, l'acide glutamique[3], peuvent être envisagés. Si, dans des essais selon le mode opératoire ordinaire (parag. 12), on ajoute une petite quantité de titane (25 γ à l'état de sel de Ti-IV) et l'un de ces acides (25 mg) on constate que ceux-ci n'empêchent pas la coloration du stilbazo par le titane. L'acide malonique a en outre le défaut d'inhiber la coloration du stilbazo avec l'aluminium. Aucun de ces réactifs n'est donc à retenir.

(14) L'acide *para*-hydroxyphénylarsinique, réactif de précipitation en milieu fortement acide du titane, peut être envisagé en vue de le complexer dans le milieu de la réaction, dont le pH est tel que la précipitation du titane par l'acide *p*-hydroxyphénylarsinique n'a pas lieu.

Dans une gamme d'essais, on met en œuvre des quantités variables de titane (jusqu'à 50 γ Ti), 25 ml de tampon (30 ml de solution d'acide acétique $M/5$ et 170 ml de solution d'acétate d'ammonium $M/5$), 5 ml de solution d'acétate d'ammonium (100 g/l), 10 ml de solution d'acide *p*-hydroxyphénylarsinique (10 g/l), 10 ml de stilbazo (0.5 g/l) et de l'eau pour compléter à 100 ml (pH du milieu final 5.5).

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* A paraître.

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La coloration augmente quand la proportion de titane croît. Ainsi il apparaît indispensable de séparer le titane. Il a été vérifié d'autre part que l'acide *p*-hydroxyphénylarsinique lui-même ne perturbe pas la réaction au stilbazo.

(15) *Séparation du titane par l'acide* p-*hydroxyphénylarsinique*

Séparer, par précipitation au moyen de ce réactif, le titane, implique que la quantité présente de celui-ci soit suffisante, des traces de titane ne précipitant qu'avec lenteur et incomplètement. C'est pourquoi l'on a mis en œuvre dans les essais ci-après 5 mg de titane, correspondant donc à une prise d'essai fictive de 1 g d'acier contenant 0.5% de Ti.

En principe l'acidité sulfurique convenable à la précipitation du titane (Ti-IV) par l'acide *p*-hydroxyphénylarsinique se situe aux environs de 1.8*N*.

Dans le cas présent, l'acidité, qui doit être aussi faible que possible (tout en assurant la précipitation totale du titane), afin qu'il ne soit pas nécessaire de neutraliser ensuite en vue du dosage colorimétrique à pH 5.6 environ, doit être déterminée.

Une dose constante de titane est précipitée par l'acide *p*-hydroxyphénylarsinique, dans différents essais, dont l'acidité est variable de l'un à l'autre. Le titane restant éventuellement en solution est mesuré par la réaction au stilbazo ellemême.

Le protocole est le suivant. Dans 5 béchers (100), distribuer:
10 ml de liqueur de titane (1 ml = 0.5 mg de Ti-IV);
respectivement 5; 10; 15; 20; 25 ml de liqueur titrée d'acide sulfurique 2*N*; 10 ml de solution d'acide *p*-hydroxyphénylarsinique; porter à commencement d'ébullition, refroidir, compléter à 50 ml en fioles jaugées. Repos (plusieurs heures). Filtrer (filtre bande bleue).

Parallèlement, préparer un essai témoin exempt de titane: 5 ml de liqueur titrée d'acide sulfurique 2*N* et 10 ml de solution d'acide *p*-hydroxyphénylarsinique (50 g/l); compléter à 50 ml en fiole jaugée.

De chacun de ces liquides, prélever 5 ml, que l'on reçoit respectivement dans 6 fioles jaugées (50 ml), compléter à ce volume avec de l'eau.

Prélever de chacun de ces liquides:
5 ml que l'on reçoit dans six fioles jaugées de 100 ml. A chacune d'elles, ajouter: le tampon, l'acétate d'ammonium et le stilbazo (parag. 13), compléter à 100 ml avec de l'eau (pH des liquides: 5.5). Mesures photométriques, avec le témoin pour réglage au zéro du photomètre.

Seul l'essai 5 ml SO_4H_2 2*N* montre que du titane a échappé à la précipitation.

Pour la suite du travail, il a été choisi: 15 ml de liqueur titrée d'acide sulfurique 2*N*, avec 10 ml de solution d'acide *p*-hydroxyphénylarsinique (50 g/l), pour le volume du liquide: 50 ml.

Il a été vérifié que des gammes à aluminium variable comportant cette séparation du titane conduisent à des résultats identiques à ceux que l'on obtient, sans cette séparation du titane et en l'absence de cet élément.

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(16) Les points suivants sont ainsi acquis:

L'acide ascorbique doit être employé pour complexer le fer, l'acide *p*-hydroxyphénylarsinique pour séparer le titane.

Soit, à titre d'exemple, la gamme suivante qui comporte:

des quantités variables d'aluminium (0 à 50 γ Al),

1 mg de Fe-III (à l'état de sulfate ferrique)

5 ml du réactif ci-après:

(15 ml de liqueur titrée d'acide sulfurique $2N$ et 10 ml d'acide *p*-hydroxyphénylarsinique, compléter à 50 ml; de ce liquide, 5 ml sont dilués à 50 ml; cette seconde dilution constitue le réactif).

20 ml de solution d'acide ascorbique (50 g/l).

25 ml de tampon (150 ml de liqueur d'acide acétique $M/5$ et 150 g d'acétate d'ammonium par litre).

10 ml de solution de stilbazo (0.5 g/l). Compléter chaque terme à 100 ml.

Mesures photométriques, le photomètre étant réglé au zéro avec l'essai témoin exempt d'aluminium.

La courbe d'étalonnage est une droite.

(17) *Aciers de nitruration*

Pour une prise d'essai de 2 mg par exemple de tels aciers, qui peuvent contenir jusqu'à 1.5% d'Al environ, soit 30 γ Al, le dosage de celui-ci pourra donc être direct.

Le mode opératoire en *appendice 2 B* a été étudié au moyen de 4 aciers au Ni (1 à 1.5%), Cr (0.7 à 3%) et Mo (0.1 à 0.35%), de nuances par suite voisines de celles des aciers de nitruration quant aux éléments d'alliage autres que l'aluminium. Des gammes d'étalonnage, comportant des doses d'aluminium atteignant 50 γ, ont permis de vérifier la validité de la méthode, et l'absence d'influence nuisible de la part du nickel, du chrome et du molybdène, dans l'ordre de grandeur des teneurs envisagées tout au moins.

En *appendice 2 A* est indiqué le mode opératoire, valable pour les aciers au titane, et qui comporte la séparation sur cathode de mercure et la séparation du titane à l'acide *p*-hydroxyphénylarsinique. Cette technique a été en particulier appliquée, avec quelques modifications de détail, à des alliages Nimonic contenant environ 2% de Ti et 1% d'Al.

(18) *Les aciers au cobalt-aluminium pour aimants*, dont la teneur en aluminium peut atteindre 20%, ne devront faire intervenir en analyse qu'une prise d'essai très petite qui n'amène que des quantités minimes de fer et d'éléments d'alliage; ils sont donc justiciables de la méthode directe de dosage de l'aluminium.

Le mode opératoire indiqué en *appendice 3* a été étudié au moyen de deux échantillons d'aciers alliés contenant respectivement Cr = 12.1%, Co = 2.4%, et

Cr = 13.8%, Co = 5%. Les gammes d'étalonnage, comportant les quantités d'aluminium prévues dans le mode opératoire, se traduisent par d'excellentes droites représentatives, et établissent ainsi en particulier que le cobalt n'a pas d'influence nuisible sur le dosage de l'aluminium au stilbazo.

(19) Des aciers inoxydables du type 18-8, dans lesquels on se proposait de doser au maximum 1% d'Al, ont été envisagés. A cette occasion l'influence perturbatrice de quantités notables de chrome, et celle de petites quantités de vanadium ont été mises en évidence.

Une prise d'essai d'un acier 18-8 de 0.5 g est attaquée par 5 ml d'acide sulfurique (1.83) au demi; neutraliser par l'ammoniaque (0.9) au demi, et précipiter le titane éventuellement présent par 15 ml de liqueur titrée d'acide sulfurique $2N$ et 10 ml de solution d'acide *p*-hydroxyphénylarsinique (50 g/l) (parag. 15), compléter à 50 ml; du filtrat prélever 5 ml que l'on dilue à 50 ml; de ce liquide, prélever cinq fois 5 ml (on opère donc sur une prise d'essai de 5 mg d'acier) que l'on reçoit en fioles jaugées de 100 ml.

Ajouter respectivement: 0-5-10-15-20 ml de liqueur type d'aluminium (1 ml = 2.5 γ Al); distribuer: 20 ml de solution d'acide ascorbique (50 g/l), 25 ml de tampon (150 ml de solution d'acide acétique $M/5$, 200 g d'acétate d'ammonium et eau q.s.p. 1 litre), 10 ml de réactif stilbazo (0.5 g/l) et de l'eau pour compléter à 100 ml.

Préparer de même une gamme témoin à partir de 0.35 g de fer pur et contenant les mêmes quantités d'aluminium dans chaque terme.

Le photomètre est réglé au zéro avec le terme 0 Al de cette gamme témoin, et au 100 avec le terme 50 γ Al de cette même gamme témoin.

On observe que tous les termes de la gamme faite avec l'acier inoxydable sont nettement plus colorés que les termes homologues de la gamme témoin, le terme 50 γ Al de la première gamme ne présentant même qu'une coloration peu supérieure à celle du terme 0 γ de cette même gamme. La nickel ne gênant pas la réaction au stilbazo, ainsi qu'il a été vérifié antérieurement à propos de l'analyse des zincs, et le titane ayant été éliminé, la cause de la perturbation doit donc être rapportée au chrome.

A remarquer que cet élément existe, dans les aciers inoxydables type 18/8, en proportion plus élevée que dans les aciers de nitruration ou dans les aciers à aimants, que la prise d'essai en analyse est largement plus grande dans le cas actuel que dans les précédents; l'on peut s'attendre à ce que l'influence du chrome y soit donc plus accusée.

Le fait a été au reste vérifié par introduction, dans des gammes de dosage, de quantités variables de chrome sous forme de sel de Cr-III: la coloration augmente bien avec la quantité de chrome en présence.

(20) La nécessité, qui se dégage ainsi, de séparer le chrome conduit à employer

l'électrolyse sur cathode mercure, au reste nécessaire pour éliminer le fer*. Mais cela entraîne à considérer l'incidence possible d'éléments, éventuellement présents dans l'acier, et qui ne seraient pas séparés de la sorte. Ce sont en particulier le vanadium, le tungstène et le zirconium.

Les deux derniers ne perturbent pas le dosage de l'aluminium au stilbazo. En revanche, le vanadium, à l'état V^{+4} ou V^{+5} donne avec le stilbazo une coloration très sensible, dans les conditions de la réaction de l'aluminium.

Il est à prévoir que tous les aciers peuvent contenir du vanadium, sinon comme élément d'addition, du moins à l'état de traces, et la sensibilité de la réaction avec cet élément est telle que des taux même inférieurs à 0.1% sont susceptibles d'entraîner une erreur par excès notable dans le dosage de l'aluminium. Il devient impossible d'accepter ce risque, spécialement dans le cas de la détermination de l'aluminium de calmage, cas où la prise d'essai d'acier en analyse est forcément élevée. Il faut donc prévoir la séparation du vanadium.

(21) *Elimination du vanadium*

Les procédés classiques de précipitation du vanadium (au vanadate de plomb ou de manganèse) ne sauraient *a priori* être envisagés dans le cas présent, vu la très faible quantité de vanadium dont il s'agit et l'influence nuisible à prévoir des réactifs introduits dans la suite du dosage.

Ont été tout d'abord essayés des réactifs organiques, puis la précipitation sous forme de silico-vanado-tungstate d'hexaméthylène-tétramine. L'échec de ces tentatives a conduit à faire usage du cupferron, par la voie de l'extraction chloroformique, qui permet la séparation du vanadium et du titane, en une seule et même opération.

(22) FIDLER[4] a indiqué que le *sulfate de dicyandiamidine* précipite, en milieu très peu acide, le vanadium à l'état de vanadate V^{+5} sous la forme du complexe $C_2H_6ON_4$, VO_3H. Selon cet auteur, la précipitation est quantitative pour de petites quantités de vanadium (inférieures au milligramme), mais des précautions doivent être prises eu égard à la solubilité notable du précipité. L'on a constaté que, si la dicyandiamidine ne gêne pas le dosage ultérieur de l'aluminium au stilbazo, en revanche la séparation du vanadium cesse d'être complète dès que le milieu de cette séparation est acidifié, même légèrement (par exemple pour une acidité $N/100$ environ): du vanadium passe dans le filtrat en quantité suffisante pour donner la coloration avec le stilbazo. En outre, une acidification assez nette du milieu est souhaitable, afin d'éviter la cause d'erreur à provenir de ce que de l'alumine peut précipiter lors de la neutralisation antérieure (qui intervient après attaque ou séparation sur cathode de mercure); cette alumine peut n'être pas redissoute par une acidification trop légère et rester sur filtre avec le complexe

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* En vue de l'électrolyse sur cathode de mercure d'aciers alliés (type 18/8 par exemple), l'acidité sulfurique du milieu doit être plus faible que dans le cas des aciers non alliés: acidité $N/10$ environ[14,15].

vanadique lors de la séparation de celui-ci par filtration. Pour ces raisons, les essais avec la dicyandiamidine n'ont pas été poussés plus avant.

(23) Le *diantipyrylphénylméthane* est indiqué par GUSEV, BEILES ET SOKOLOVA[5] en vue de la précipitation du vanadium (V^{+5}) sous la forme:

$$[(C_{11}H_{11}ON_2)_2 — CH\text{-}C_6H_5]_2\, V_6O_{17}H_4$$

et du dosage du vanadium dans les ferrovanadiums.

Le mémoire original, qui décrit d'ailleurs la préparation du réactif, au reste aisée, indique que la précipitation du V^{+5} à l'état de vanadate doit être faite en milieu très faiblement acide: milieu environ centinormal en acide nitrique. L'on a observé que cette acidité nitrique est encore trop élevée pour que la précipitation du vanadium soit totale, et qu'il en est de même pour une acidité sulfurique conférée par 1 à 5 ml d'une liqueur titrée d'acide sulfurique *N* pour un volume total de 125 ml. Ainsi, dans un tel milieu, la précipitation de 2.5 mg de V (à l'état de vanadate) par 10 ml de solution alcoolique à 20 g/l du réactif (qui, par lui-même ne gêne pas la réaction de l'aluminium au stilbazo) laisse subsister suffisamment de vanadium pour que le dosage ultérieur de l'aluminium au stilbazo en soit largement perturbé; la coloration augmente d'ailleurs avec la quantité de vanadium initialement introduite: la perturbation est donc bien due au vanadium et celui-ci échappe en partie à l'action du réactif. Diminuer l'acidité du milieu afin de rendre la séparation du vanadium totale exposerait aux causes d'erreurs mêmes déjà mentionnées pour la dicyandiamidine. Le diantipyrylphénylméthane est donc à abandonner le cas présent.

(24) *L'α-benzoinoxime* est un réactif microchimique du vanadium (vanadates), avec lequel il donne un précipité jaune (WEST ET CONRAD[6]).

Il a pu être observé que l'α-benzoïnoxime ne gêne ni la séparation ultérieure du titane à l'acide *p*-hydroxyphénylarsinique, ni le dosage colorimétrique de l'aluminium au stilbazo, que la précipitation du vanadium (5 mg V à l'état de vanadate) est complète, au moyen de 10 ml de solution alcoolique d'α-benzoïnoxime (20 g/l), en milieu acidifié par 1 ml de liqueur titrée d'acide sulfurique *N* pour un volume total de 25 ml.

Le mode opératoire applicable aux aciers serait donc le suivant:
Attaque de 1 g d'acier (pour l'étude de la méthode, à une prise d'essai de fer pur de 1 g, ajouter 2.5 mg de V et 5 mg de Ti), électrolyse sur cathode de mercure. Le liquide résultant, concentré à petit volume, est neutralisé, acidifié pour 1 ml par 1 ml de liqueur titrée d'acide sulfurique *N*, oxydé par le persulfate d'ammonium (il faut en effet prévoir que le vanadium est au stade VO^{+2} après électrolyse), l'on précipite le vanadium par l'α-benzoïnoxime, et complète à 25 ml. Du filtrat, une partie aliquote de 20 ml sert à précipiter le titane, le liquide final étant complété à 50 ml (parag. 15). Du filtrat, une partie aliquote de 5 ml est complétée à 50 ml.

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Les dosages colorimétriques sont faits à l'aide de ce dernier liquide (5 ml de celui-ci, que l'on reçoit en fioles jaugées de 100 ml). Si l'on a opéré initialement avec un fer pur, ajouter à ces liquides des doses variables d'aluminium (0 à 50 γ Al) pour l'obtention d'une gamme d'étalonnage. Dans chaque essai, il est ajouté 20 ml de solution d'acide ascorbique (50 g/l), 25 ml de tampon (150 ml d'acide acétique $M/5$, 200 g d'acétate d'ammonium et eau q.s.p. 1 litre), 10 ml de réactif stilbazo (0.5 g/l) et de l'eau pour compléter à 100 ml.

Les mesures photométriques sont faites par rapport à un témoin (fer pur), mené comme ci-dessus, et exempt de vanadium, de titane, et d'aluminium.

Les gammes obtenues sont bien échelonnées, le vanadium et le titane ont bien été séparés.

Toutefois, ce mode opératoire comporte, en application à des aciers, deux écueils: tout d'abord, celui, déjà cité (parag. 22 et 23) de la très faible acidité du milieu, après neutralisation, en vue de la précipitation par l'*α*-benzoïnoxime; ensuite du bioxyde de titane précipite par hydrolyse lors de l'oxydation du vanadyle par le persulfate, dans le milieu peu acide où a lieu cette oxydation; et lors de la séparation ultérieure du titane par l'acide *p*-hydroxyphénylarsinique, si la quantité de titane qu'apporte l'acier est faible, la plus grande partie en est séparée par cette hydrolyse et il n'en reste plus suffisamment pour que la précipitation de ce reliquat, par l'acide *p*-hydroxyphénylarsinique, soit totale (parag. 15). Il a pu être observé que le liquide, obtenu dans de telles conditions de séparation du titane, peut être pollué par celui-ci, et des résultats erronés par défaut se produisent alors.

Pour cette raison, l'emploi de l'*α*-benzoïnoxime pour séparer le vanadium n'a pas été retenu.

(25) La combinaison du vanadium sous la forme de *silico-vanado-tungstate* donne naissance à des composés susceptibles de précipiter avec les bases organiques (hexaméthylène tétramine dans le cas présent) et dans cette séparation d'entraîner l'acide titanique résultant de l'hydrolyse du sel titanique en présence dans le milieu. Dans des circonstances analogues en effet, cette observation a antérieurement été faite[7]. Ainsi serait obtenue à la fois l'élimination du vanadium et du titane.

Les silico-vanado-tungstates ne paraissent pas avoir été étudiés jusqu'ici. Les phospho-vanado-tungstates, qui constituent en particulier le principe de méthodes classiques de dosage du phosphore et du vanadium, dans les aciers, sont étudiés quant à leur constitution par CANNERI[8], et l'on peut admettre que les dérivés du silicium suivent des lois analogues aux leurs. Ces complexes résultent du remplacement de radicaux W_2O_7 par des radicaux V_2O_6 (2 à 4) dans le noyau central.

A remarquer que CANNERI écrit les phospho-vanado-tungstates selon la formule de composés de la série 12:

$P[(W_2O_7)_4(V_2O_6)_2](NH_4)_6H$, donc hepta-acides; or, on sait que les phosphotungstates de la série 12 sont tri-acides. Il est hautement probable que les substances obtenues par CANNERI n'appartiennent pas à la série 12, mais à une série moins condensée, donc hydrolysée, ce qui explique l'exaltation de l'acidité. Il ne sera pas discuté de la constitution exacte de ces complexes, cette préoccupation sortant du cadre du travail actuel.

(26) Quant à la forme du vanadate entrant dans le complexe, celle-ci doit au contraire être considérée.

On sait en effet (SOUCHAY ET CARPENI[9], DUCRET[10]) que, par acidification légère, les solutions d'orthovanadates prennent une coloration jaune-orangé, qui disparaît plus ou moins avec le temps, et selon le pH du milieu.

(27) L'expérience montre que des solutions de vanadates ($M/20$ en orthovanadate), acidifiées par des quantités variables, d'un essai à l'autre, d'acide sulfurique dilué ($10N$; N; $N/10$; $N/100$; $N/1000$ selon les essais) sont jaunes à partir de pH 8.6 et jusqu'à pH 2 environ, mais qu'à des acidités supérieures (pH 2 à 0.5) la coloration disparaît en quelque temps.

Or il a été observé que, dans la formation du silico-vanado-tungstate, le liquide est jaune lorsque la forme du vanadate est elle-même jaune, et qu'alors, après précipitation par l'hexaméthylène-tétramine, les filtrats sont également jaunes. Du vanadium a donc échappé à la précipitation. Au contraire, si l'acidité lors de la formation du vanadate est telle que le liquide du silico-vanado-tungstate soit incolore, il n'échappe plus, lors de la précipitation de l'hexaméthylènetétramine, de vanadium, que l'on n'en décèle plus par la réaction au stilbazo; les réactifs intervenant dans la constitution du complexe (silicate, tungstate, hexaméthylènetétramine) sont d'autre part, ainsi qu'il a été vérifié, sans action sur la réaction au stilbazo elle-même.

(28) Les conditions d'acidité ont donc été réglées selon le protocole ci-après.

A 5 ml d'une solution de chlorure de vanadyle (1 ml = 0.5 mg de V, correspondant, pour une prise d'essai hypothétique de 1 g d'acier, à 0.25% de V de l'acier) ajouter: 5 ml de liqueur titrée d'acide sulfurique N, 5 ml de solution de sulfate de sodium (100 g/l), 10 ml de solution de persulfate d'ammonium (10 g/l), porter à l'ébullition: le vanadyle est ainsi oxydé au stade du vanadate. Refroidir, ajouter 5 ml de solution de silicate de sodium (1.25 g/l, qualité cristallisé très soluble R.P.). Porter à l'ébullition. Ajouter 5 ml de solution de tungstate de sodium (17 g/l), porter à l'ébullition. Refroidir, transvaser en fiole jaugée de 50 ml, ajouter 5 ml de liqueur titrée d'acide sulfurique $N/10$ et 2 ml de solution d'hexaméthylènetétramine (250 g/l), et compléter enfin à 50 ml avec de l'eau. Repos plusieurs heures, filtrer. Le pH du milieu incolore est 2.35 à 2.4.

Du filtrat, prélever 5 ml que l'on complète à 50 ml en fiole jaugée. De ce liquide, prélever 5 ml que l'on reçoit en fiole jaugée de 100.

Ajouter 10 ml de solution d'acide ascorbique (50 g/l), 25 ml de tampon (150 ml d'acide acétique $M/5$, 150 g d'acétate d'ammonium, par litre), 10 ml de solution de stilbazo (0.5 g/l) et compléter à 100 ml avec de l'eau (pH du milieu final 5.7).

Mesures photométriques par rapport à un témoin, fait de la même façon, mais exempt de vanadium. Trouvé dans divers essais: 3 divisions au maximum du photomètre.

La totalité du vanadium a donc bien entré dans le complexe et a été pratiquement éliminée.

(29) Il a été tenté de contrôler que l'acide vanadique entre bien dans un complexe silico-vanado-tungstique, par la voie *polarographique*.

L'acide silico-tungstique (SOUCHAY[11]) donne, en milieu tampon acéto-acétique avec le sulfate de sodium comme électrolyte support, des polarogrammes qui présentent les paliers suivants. Vers 0.5 volt, un premier palier, caractéristique de la série 12; puis vers 0.75 volt un second palier; enfin, au delà de 1 volt un troisième palier. A mesure que croît le pH, la grandeur de chacun de ces paliers décroît, le potentiel du premier tend à diminuer et le troisième disparaît; l'alcalinisation croissante a pour effet d'hydrolyser l'acide silico-12-tungstique en acide silico-11-tungstique, et l'allure générale de la courbe polarographique est modifiée; les paliers relatifs à l'acide de la série 11 sont beaucoup moins marqués que ceux relatifs aux composés de la série 12.

Le polarogramme que représente la courbe 5 de la Fig. 2 a été obtenu avec 0.3 g d'acide silico-tungstique cristallisé, polarographié en milieu acéto-acétique (pH 3.54) et en présence de sulfate de sodium comme électrolyte support; il est bien comparable à ceux qu'indique SOUCHAY[11]. L'acide silico-tungstique, obtenu au moyen de l'acide silicique et de l'acide tungstique dans le milieu d'acidité sulfurique indiqué dans le précédent paragraphe, conduit aux polarogrammes qu'indique la Fig. 2. Ceux-ci ont été tracés pour différents pH dans les milieux suivants: formation de l'acide silico-tungstique à l'aide de 5 ml de solution de silicate de sodium (0.5 g/l) et de 20 ml de solution de tungstate de sodium (17 g/l) en présence de 5 ml de liqueur titrée d'acide sulfurique *N*; addition d'un volume variable d'un essai à l'autre, de liqueur titrée de soude *N*, de 10 ml de liqueur d'acide acétique *N*, de 20 ml de solution de sulfate de sodium (100 g/l) et de l'eau pour compléter à 100 ml.

Ces polarogrammes (1 à 4 Fig. 2) montrent des paliers estompés et se rapprochent de ceux qu'indique SOUCHAY[11]* pour l'acide de la série 11: ce sont donc des acides silico-tungstiques moins condensés que ceux de la série 12, et appartenant très probablement à la série 11.

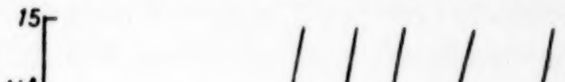

Fig. 2. Chaque courbe est décalée de 0.25 v par rapport à la précédente. Acide silicique + acide tungstique. Electr. SO_4Na_2, tampon acétique.

(30) La réduction polarographique de l'acide orthovanadique est faite par LINGANE[12] en milieu sulfurique *N*/20 et *N*/10 en chlorure de potassium, ou également en milieu chlorhydrique normal: il s'agit de la vague V (IV)→ V (II), car le mercure, à lui seul et sans courant de polarisation, réduit l'acide vanadique au stade du sel de vanadyle et l'obtention de la vague complète correspondant à cette réduction n'est pas possible.

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* *Cf.* SOUCHAY[11] p. 112.

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Le milieu tamponné par l'acétate, contenant 5 ml de liqueur titrée d'acide sulfurique *N* et avec 10 ml de solution de sulfate de sodium (100 g/l) comme électrolyte support, donne un polarogramme exempt de vague parasite avant — 1.25 volt, donc qui laisse une plage de potentiel suffisante pour que s'y inscrive la vague du vanadium (Fig. 3). Avec un tel milieu de fond, une vague débutant dès le potentiel O est obtenue lorsque l'on fait intervenir l'acide vanadique (5 ml de solution de chlorure de vanadyle à 1 ml = 0.5 mg de V, 10 ml de solution de persulfate d'ammonium (10 g/l) et 5 ml de liqueur titrée d'acide sulfurique *N*; ébullition; 10 ml de solution de sulfate de sodium 100 g/l et tampon acétique). Une seule vague est obtenue (Fig. 4), qui est très vraisemblablement celle de l'acide vanadique (V(V)→V(IV)) et qui présente un maximum très net; LINGANE signale en effet un tel maximum dans la vague V(V)→V(IV). Dans la même hypothèse, la seconde vague, vers 1.25 V, est celle de la réduction du vanadyle (V(IV)→V(II)).

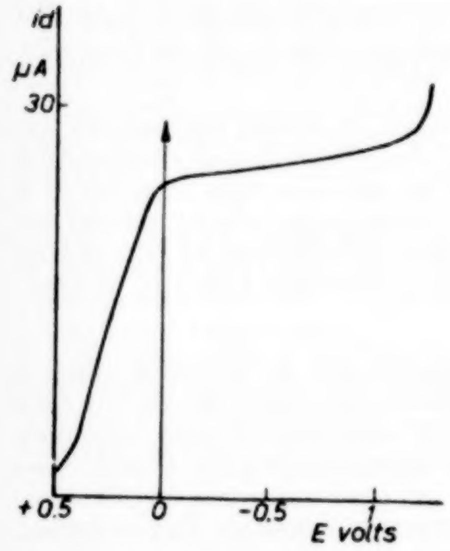

Fig. 3. Support: 6ml SO_4H_2 *N* + 10 ml SO_4Na_2 (100 g/l) + 10 ml acide acétique *N* + 3 ml acétate Na *N*.

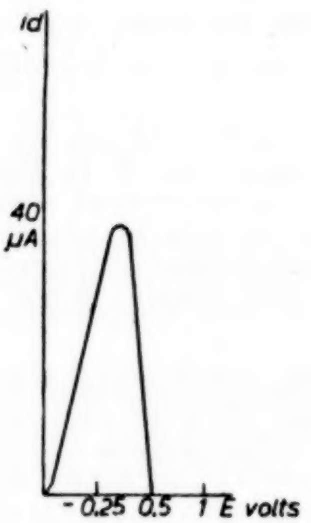

Fig. 4. 2.5 mg V(IV) oxydé par $S_2O_8(NH_4)_2$. Milieu SO_4Na_2 et tampon acéto-acétique.

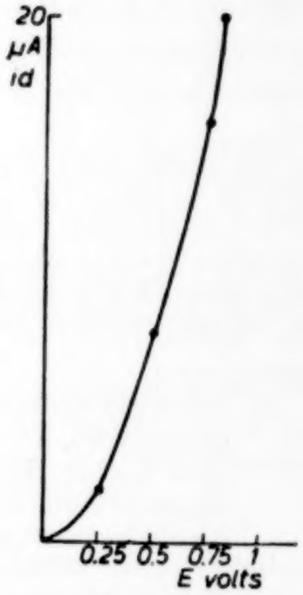

Fig. 5. Si-V-W. 2.5 mg V(IV) oxydé par persulfate, milieu sulfurique, tampon acéto-acétique.

(31) Le silico-vanado-tungstate, obtenu dans la présente étude (parag. 28) devrait donner un polarogramme analogue à celui de l'acide silico-tungstique (Fig. 2) si l'acide vanadique est bien complexé à l'état d'acide silico-vanado-tungstique, ou bien la superposition des polarogrammes de l'acide silico-tungstique et de l'acide vanadique, si la combinaison n'a pas lieu.

Sont mis en présence: 5 ml de solution de chlorure de vanadyle (1 ml = 0.5 mg de V), 5 ml de liqueur titrée d'acide sulfurique *N*, 5 ml de solution de persulfate d'ammonium (10 g/l); ébullition; 5 ml de solution de sulfate de sodium (100 g/l), 5 ml de solution de silicate de sodium (0.5 g/l), 20 ml de solution de tungstate de sodium (17 g/l), le tampon acéto-acétique conférant au milieu le pH 2 environ, et l'on complète à 100 ml. Le polarogramme se rapproche de ceux de l'acide silico-tungstique, sans qu'apparaisse la vague de vanadate. La seule conclusion possible est que le vanadium a bien été complexé sous la forme de l'hétéropolyacide tungstique, et que ce complexe n'appartient très vraisemblablement pas, vu l'absence de paliers, à la série 12, mais à une série moins condensée (série 11 ou inférieure) (*cf.* parag. 25).

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(32) Il résulte donc de l'étude polarographique que la combinaison de l'acide vanadique à l'acide silico-tungstique aboutit bien à un complexe dans lequel le vanadium est combiné, et des essais relatés au paragraphe 28 que la totalité du vanadium mis en jeu est bien précipitée sous la forme de la combinaison insoluble de ce complexe avec l'hexaméthylène tétramine.

(33) Si du *titane* (1 ml de solution de sel titanique = 5 mg de Ti, soit 0.5% de Ti pour une prise d'essai hypothétique de 1 g d'acier; cette solution de titane est obtenue par dilution de la solution commerciale de trichlorure de titane à 15%) est mis en oeuvre avec le vanadium, dans l'essai indiqué parag. 28, l'on constate une coloration parasite dans la réaction ultérieure au stilbazo. Le vanadium ayant bien été éliminé, reste le titane à l'influence duquel cette perturbation doit être rapportée. Le titane mis en présence n'aurait donc pas été totalement précipité par hydrolyse, et il doit être éliminé pour son propre compte.

Un essai comportant vanadium et titane est mené selon le mode opératoire ci-dessus (parag. 28). A 40 ml du filtrat de la séparation du silico-vanado-tungstate d'hexaméthylène tétramine (antérieurement complété à 50 ml) que l'on concentre à 20 ml environ: ajouter 15 ml de liqueur titrée d'acide sulfurique $2N$ et 10 ml de solution d'acide *p*-hydroxyphénylarsinique (50 g/l). Porter à l'ébullition et compléter le liquide froid à 50 ml en fiole jaugée; laisser reposer (plusieurs heures), filtrer.

Deux cas:

a) Prélever 20 ml du liquide que l'on reçoit en fiole jaugée de 50 ml, compléter à ce volume. De ce liquide, prélever cinq prises d'essai aliquotes de 10 ml que l'on reçoit dans cinq fioles jaugées de 100 ml. A chacune d'elles, ajouter respectivement: 0; 5; 10; 15; 20 ml de liqueur d'aluminium ($2.5\ \gamma$ ml). Les mesures porteront ainsi au maximum sur 0.05% d'Al de l'acier hypothétique.

b) Prélever 10 ml du liquide, compléter à 50 ml et continuer selon a). Les mesures porteront ainsi sur 0.1% d'Al au maximum de l'acier.

Dans un cas comme dans l'autre, la réaction colorée est faite dans chacun des essais suivants: 20 ml de solution d'acide ascorbique (50 g/l), 25 ml de tampon (150 ml de solution d'acide acétique $N/5$ et 200 g d'acétate d'ammonium); 10 ml de solution au stilbazo (0.5 g/l) et de l'eau pour compléter à 100 ml. Mesures photométriques par rapport à des témoins exempts de vanadium, de titane et d'aluminium.

(34) Les résultats des mesures photométriques montrent que les termes O de chacune de ces deux gammes contenant vanadium et titane, sans aluminium, sont plus colorés que le témoin exempt de ces éléments; les gammes elles-mêmes, quoique assez bien échelonnées, présentent des intensités de coloration trop élevées par rapport à celles qui devraient exister, en l'absence de vanadium et de titane.

Si donc le titane a bien été partiellement éliminé lors de la précipitation du silico-vanado-tungstate, il n'en subsiste plus dans le filtrat de cette séparation suffisamment pour que ce reliquat précipite totalement par l'acide *p*-hydroxyphénylarsinique (*cf.* parag. 15). D'où l'idée de séparer le titane avant le vanadium.

(35) A des quantités de vanadium et de titane, identiques à celles de l'essai précédent (parag. 28 et 33), ajouter: 15 ml de liqueur titrée d'acide sulfurique $2N$ et 10 ml de solution d'acide *p*-hydroxyphénylarsinique (50 g/l), compléter à 50 ml. A 40 ml du filtrat sont ajoutés: 5 ml de solution de persulfate d'ammonium (20 g/l) et l'on porte à l'ébullition; refroidir, neutraliser par la soude ($2N$), acidifier immédiatement par 5 ml de liqueur titrée d'acide sulfurique $2N$ et ajouter les réactifs: 5 ml de solution de silicate de sodium 1.25 g/l; 5 ml de solution de tungstate

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de sodium 17 g/l; ébullition; 10 ml de liqueur titrée d'acide sulfurique *N*/10 et 2 ml de solution d'hexaméthylène tétramine 250 g/l). Compléter à 100 ml en fiole jaugée. Filtrer après repos (pH de ce liquide = 2.4.

Une partie aliquote de 80 ml du filtrat est complétée à 100 ml. De ce liquide, prélever cinq prises d'essai de 10 ml chacune, et 5 prises d'essai de 5 ml chacune que l'on reçoit en fioles jaugées de 100 ml. A chacune de ces cinq prises d'essai de l'une et l'autre séries (série 10 et série 5 ml), ajouter respectivement 0; 5; 10; 15; 20 ml de liqueur d'aluminium (2.5 γ ml Al). Les mesures portent ainsi sur 0.05 et 0.1% d'Al respectivement, pour une prise d'essai hypothétique de 1 g d'acier, comme dans l'expérimentation précédente (parag. 33).

Des essais semblables sont faits en ajoutant, dès le départ, avec le vanadium et le titane, des quantités d'aluminium échelonnées, telles qu'elles correspondent au maximum à 0.05% d'Al et 0.1% d Al de l'acier hypothétique (dont prise d'essai supposée: 1 g), pour les parties aliquotes finales de 5 et 10 ml du liquide destiné aux mesures colorimétriques.

Celles-ci comportent les additions de: 10 ml de solution d'acide ascorbique (50 g/l); 25 ml de tampon (150 ml de solution d'acide acétique *N*/5, 150 g d'acétate d'ammonium et de l'eau pour compléter au litre); 10 ml de solution de stilbazo (0.5 g/l) et de l'eau pour compléter à 100 ml.

Toutes les mesures colorimétriques sont faites après réglage au zéro du photomètre avec un des témoins exempts de vanadium, de titane et d'aluminium, et comportant 5 ou 10 ml du liquide prélevé *in fine*, selon la série envisagée.

(36) Il a été constaté que la précipitation du vanadium est fortement empêchée, le précipité est anormalement peu abondant. Les réactifs de précipitation du titane, c'est-à-dire l'acide *p*-hydroxyphénylarsinique, inhibent donc la précipitation du complexe vanadique.

Les colorations des termes exempts d'aluminium, mais avec vanadium et titane sont trop intenses comparativement aux témoins exempts de ces additions, et les gammes dans leur ensemble trop colorées. Il faut donc rattacher cette perturbation à la séparation défectueuse du vanadium, lequel réagit avec le stilbazo.

(37) Les difficultés rencontrées dans les modes de séparation du titane et du vanadium ci-dessus relatées conduisent à envisager d'autres réactifs:

le *cupferron*, réactif classique du titane, est également un réactif du vanadium à l'état V(V) ou V(IV)[13]. La séparation par extraction chloroformique s'applique dans ce cas.

(38) *Détermination de l'optimum d'acidité pour la séparation du titane au cupferron*

a) Dans une série d'ampoules à décantation (100), verser successivement: 1 ml de solution de titane (1 ml = 5 mg de Ti) obtenue par dilution au dixième environ de la solution commerciale de trichlorure de titane à 15/100; 1 ml de cette solution correspond à 0.5% de Ti de l'acier, dont la prise d'essai serait 1 g; oxyder la prise d'essai de solution de titane, soit 1 ml, par une à deux gouttes d'eau oxygénée à 1 vol.); des quantités variables (5 à 25 ml) de liqueur titrée d'acide sulfurique 2*N* et des quantités variables et correspondantes d'eau (25 à 5 ml) afin de réaliser les mêmes dilutions; 5 ml de solution de sulfate de sodium (100 g/l) et 5 ml de solution de cupferron (50 g/l). Ajouter 10 ml de chloroforme et extraire. Répéter encore trois fois cette extraction. Les liquides aqueux de chaque essai sont neutralisés au moyen d'une liqueur de soude 2*N*, afin d'obtenir uniformément la même acidité en vue des mesures colorimétriques. Compléter chacun de ces essais à 100 ml en fioles jaugées.

b) De chacune de celles-ci, prélever 10 ml que l'on reçoit en fioles jaugées de 100 ml et ajouter successivement: 10 ml de solution d'acide ascorbique (50 g/l);

25 ml de tampon (150 ml d'acide acétique $N/5$ et 150 g d'acétate d'ammonium, par litre); 10 ml de réactif stilbazo (0.5 g/l) et de l'eau pour compléter chaque essai à 100 ml.

c) Mesures photométriques par rapport à un essai à blanc obtenu en diluant 5 ml de liqueur titrée d'acide sulfurique $2N$ à 100 ml; prélever 10 ml que l'on reçoit en fiole jaugée de 100 et ajouter successivement l'acide ascorbique, etc. . . (*cf.* b, ci-dessus).

d) Lors de ces mesures photométriques, faites en réglant à zéro le photomètre au moyen de l'essai à blanc c), le terme 5 ml d'acide sulfurique $2N$ se montre identique à cet essai à blanc. Les colorations des autres essais, qui vont en croissant discrètement, montrent que dans ceux-ci tout le titane n'a pas été éliminé.

L'optimum d'acidité pour l'extraction du titane au *cupferron* est donc: 5 ml de liqueur titrée d'acide sulfurique $2N$. Ce résultat est au reste favorable: c'est en effet à cette acidité que tous les liquides résultant de l'extraction ont été ramenés en vue des mesures photométriques.

(39) *Extraction du vanadium par l'α-benzoïnoxime*

Ce réactif, déjà essayé pour la précipitation du vanadium V(V) en milieu faiblement acide (parag. 24) a été appliqué par le moyen de l'extraction chloroformique, dans lequel le complexe vanadique est soluble. Le danger de perte d'alumine éventuellement précipitée en milieu très peu acide cesse semble-t-il de se présenter dans le cas actuel, aucune filtration du complexe vanadique n'intervenant plus. Les essais ont été faits selon la méthode ci-après.

a) A 5 ml de solution de chlorure de vanadyle (1 ml = 0.5 mg de V) ajouter 1 ml de liqueur titrée d'acide sulfurique N, 5 ml de solution de sulfate de sodium (100 g/l) 10 ml de solution de persulfate d'ammonium (10 g/l), 10 ml d'eau. Ebullition. Transvaser en ampoule à décantation (100), ajouter 10 ml de réactif alcoolique à l'α-benzoïnoxime (20 g/l) et extraire successivement trois fois avec 10 ml de chloroforme pour chacune d'elles. Afin de séparer du titane supposé, au liquide aqueux, sont ajoutés: 5 ml de liqueur titrée d'acide sulfurique $2N$, 5 ml de solution de cupferron (50 g/l), et l'on procède à 4 extractions successives au moyen de 10 ml de chloroforme pour chacune d'elles. Le liquide aqueux est complété à 100 ml en fiole jaugée. Au moyen d'un prélèvement de 10 ml, on opère la réaction et le dosage colorimétrique.

Un même essai comporte, outre le vanadium, 1 ml de solution de titane (Ti(IV)) (1 ml = 5 mg de Ti). Enfin un essai semblable (témoin) ne comporte ni titane ni vanadium.

Les mesures colorimétriques de l'essai comportant vanadium, ou titane et vanadium, sont identiques à celle du témoin: le titane et le vanadium ont donc bien été séparés.

b) Essais avec aluminium.

A 5 prélèvements de 10 ml du liquide *témoin* (exempt de vanadium et de titane), résultant des extractions chloroformiques, sont ajoutés respectivement: 0; 5; 10; 15; 20 ml de liqueur d'aluminium (1 ml = 2.5 γ Al).

Opérer de même avec le liquide, résultant des extractions chloroformiques, de l'essai avec vanadium seul, et de celui fait avec vanadium et titane.

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Opérer les réactions colorées et les mesures photométriques pour chacune de ces trois gammes, le photomètre étant réglé au zéro à l'aide du terme O Al de la gamme témoin (exempte de V et de Ti), et à 100 à l'aide du terme 100 Al de la même gamme.

La gamme témoin, la gamme avec vanadium, et la gamme avec vanadium et titane, sont bien identiques.

(40) Dans les essais suivants l'aluminium est ajouté en même temps que le vanadium et le titane: vérification est ainsi faite que les séparations n'entraînent pas des pertes en aluminium.

a) En ampoule à décantation (100), ajouter 20 ml d'une liqueur titrée d'aluminium à 25 γ/ml Al (soit 500 γ Al), 1 ml de liqueur titrée d'acide sulfurique *N*, 5 ml de solution de sulfate de sodium (100 g/l) 10 ml de réactif alcoolique à l'α-benzoïnoxime (20 g/l). Trois extractions successives, au moyen de 10 ml de chloroforme pour chacune d'elles. Au liquide aqueux, ajouter 5 ml de liqueur titrée d'acide sulfurique 2*N* et 5 ml de solution de cupferron (50 g/l). Quatre extractions par 10 ml de chloroforme chacune. Le liquide aqueux est complété à 100 ml en fiole jaugée. Mesure colorimétrique sur partie aliquote de 10 ml (contenant donc 50 γ Al) (parag. 38-b).

b) L'essai précédent est répété, en omettant seulement l'addition de cupferron et les extractions chloroformiques afférentes.

c) L'essai a) est répété en omettant l'addition d'α-benzoïnoxime et les extractions chloroformiques afférentes.

d) Témoin: en fiole jaugée de 100 ml, ajouter successivement: 250 γ Al, 1 ml de liqueur titrée d'acide sulfurique *N*, 5 ml de liqueur titrée d'acide sulfurique 2*N*, 5 ml de solution de sulfate de sodium (100 g/l). Compléter à 100 ml. Mesure colorimétrique sur 10 ml de ce liquide (parag. 38-b).

Les *résultats* de ces mesures:

a: 46 divisions du photomètre; b: 46 divisions; c: 45 divisions et d (témoin) 46 divisions, montrent que les réactifs eux-mêmes ne conduisent à aucune perte en aluminium.

e) Gamme à aluminium variable, en présence de vanadium et de titane.

A 5 ml de solution vanadylique (1 ml = 0.5 mg de V), en bécher 100 ajouter: 5 ml de solution de sulfate de sodium (100 g/l); 0.5 ml de liqueur titrée d'acide sulfurique *N*, 10 ml de solution de persulfate d'ammonium (10 g/l) et porter à ébullition.

D'autre part, dans un tube à essai, à 1 ml de solution de tétrachlorure de titane (1 ml = 5 mg de Ti) ajouter 0.5 ml de liqueur titrée d'acide sulfurique *N*, et goutte à goutte de l'eau oxygénée jusqu'à décoloration. Porter rapidement à courte ébullition.

Ces deux opérations portant sur les solutions de vanadyle, et de titane sont épétées en quatre exemplaires. Dans quatre ampoules à décantation (de 100), distribuer: 5-10-15-20 ml de liqueur d'aluminium (25 γ/ml d'Al), soit 125-250-375 et 500 γ Al, puis, dans chacune d'elles, les préparations ci-dessus de titane et de vanadium. Ajouter 10 ml de réactif alcoolique — α-benzoïnoxime (20 g/l); trois extractions par 10 ml de chloroforme. Au liquide aqueux, ajouter 5 ml de solution de cupferron (50 g/l); quatre extractions par 10 ml de chloroforme. Compléter les liquides aqueux à 100 ml en fioles jaugées, et, à l'aide de 10 ml de chacun d'eux, opérer la réaction colorimétrique (parag. 38-b).

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Les quantités d'aluminium ainsi mises en oeuvre sont égales à celles que mettait en oeuvre la gamme précédente exempte de titane et de vanadium (parag. 39b) où l'aluminium était ajouté après séparation fictive du vanadium et du titane. Le photomètre étant réglé au moyen du terme témoin (exempt d'aluminium) de cette gamme (parag. 39b), les densités optiques des quatre essais ci-dessus sont mesurées. Comparativement aux essais de la gamme (parag. 39b), contenant des quantités d'aluminium égales, ces quatre essais sont tous erronés par défaut.

Les pertes en aluminium sont à rapporter à une précipitation d'alumine, dans le milieu peu acide de la séparation à l'α-benzoïnoxime (*cf.* parag. 22).

(41) Le vanadium tri- ou pentavalent, est, comme le titane susceptible de précipiter avec le cupferron, mais les conditions d'acidité ne sont pas connues exactement[13] et doivent être déterminées.

a) Dans une série de 8 ampoules à décantation, verser successivement:

5 ml de solution de chlorure de vanadyle (1 ml = 0.5 mg de V; 5 ml de solution de sulfate de sodium (100 g/l); des volumes variables de liqueur titrée d'acide sulfurique 2*N* (5-10-15 etc... 50 ml) et d'eau telles que le volume total (acide + eau) soit 50 ml; 5 ml de solution de cupferron (50 g/l). Trois extractions par 10 ml chacune de chloroforme. Les liquides aqueux sont neutralisés par une liqueur titrée de soude 2*N*, réacidifiés par 5 ml de liqueur titrée d'acide sulfurique 2*N* et complétés à 100 ml en fioles jaugées.

Un essai à blanc B, sans vanadium ni titane, comporte 10 ml de liqueur titrée d'acide sulfurique 2*N*, que l'on traite selon le mode opératoire ci-dessus (introduction du sulfate de sodium, 40 ml d'eau, le cupferron, extraction chloroformique, etc...).

Enfin l'essai ***témoin*** est préparé par dilution de 5 ml de liqueur titrée d'acide sulfurique 2*N* à 100 ml en fiole jaugée.

De chacun de ces 10 essais, en fioles jaugées (100), 10 ml sont prélevés et servent à la mesure colorimétrique (parag. 38-b). Les mesures photométriques sont faites après réglage du photomètre au zéro à l'aide du ***témoin***.

Résultats obtenus:

	ml SO_4H_2 $2N$:							
T	5	10	15	25	25	30	40	50
	mesures photomériques, divisions du photomètre:							
O	0	3	3		4	7	10	14

Ainsi, l'acidité conférée par 5 ml de liqueur titrée d'acide sulfurique 2*N*, identique d'ailleurs à celle trouvée pour le titane dans la même extraction (parag. 38), convient pour la séparation du vanadium-IV par le cupferron.

b) Un essai identique aux précédents, mais comportant l'introduction avec le vanadium à l'état de sel de vanadyle, de 1 ml de solution de titane (1 ml = 5 mg de Ti) montre que, avec cette même acidité, le vanadium-IV et le titane-IV sont bien éliminés et ne donnent plus la coloration avec le stilbazo; à remarquer que les stades d'oxydation (vanadyle et titane-IV) sont bien ceux auxquels aboutira l'électrolyse sur cathode de mercure, du milieu d'attaque de l'acier.

(42) Gammes avec aluminium variable, comportant la séparation du vanadium et du titane au ***cupferron***.

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a) Dans une ampoule à décantation (100) introduire successivement:

5 ml de solution de chlorure de vanadyle (1 ml = 0.5 mg de V) (ne pas oxyder au persulfate); 1 ml de solution de trichlorure de titane (1 ml = 5 mg de Ti) (oxyder au préalable par l'eau oxygénée à 1 vol. parag. 40-e); 5 ml de solution de sulfate de sodium (100 g/l); 5 ml de liqueur titrée d'acide sulfurique $2N$; 25 ml d'eau; et 5 ml de solution de cupferron (50 g/l). Quatre extractions successives par 10 ml de chloroforme. Compléter à 100 ml les liquides aqueux en fioles jaugées.

b) *Essais témoins.* Dans une ampoule à décantation (100) ajouter successivement: 5 ml de solution de sulfate de sodium (100 g/l); 5 ml de liqueur titrée d'acide sulfurique $2N$; 30 ml d'eau, et 5 ml de solution de cupferron (50 g/l). Quatre extractions successives par 10 ml de chloroforme. Compléter à 100 ml le liquide aqueux en fiole jaugée (100).

Du liquide a) (en fiole jaugée de 100) prélever cinq fois 10 ml, que l'on reçoit en fioles jaugées (de 100). Distribuer: 0, 5, 10, 15, 20 ml de liqueur d'aluminium (1 ml = 2.5 γ Al).

Du liquide b) (*témoin*) (en fiole jaugée de 100), prélever cinq fois 10 ml que l'on reçoit en fioles jaugées (de 100). Distribuer les mêmes quantités d'aluminium que pour le liquide a).

Mesures colorimétriques (parag. 38-b), l'essai 0 Al de la gamme *témoin* b) servant pour le réglage au zéro du photomètre, et l'essai 20 ml de solution d'aluminium de cette gamme b) servant pour le réglage à 100 du photomètre.

Tous les termes des gammes a et b sont ensuite mesurés, l'appareil ainsi réglé.

Des liquides a) et b) (en fioles jaugées de 100) on prélève cinq fois 5 ml et l'on ajoute l'aluminium comme en a et b aux mesures colorimétriques (parag. 38-b), et l'on procède comme ci-dessus. On obtient deux nouvelles gammes, a′ et b′ faites avec 5 ml seulement (et non plus 10 ml) du liquide d'extraction du vanadium et du titane. L'essai zéro de la gamme témoin b′) sert pour le réglage du photomètre du zéro, et l'essai 50 γ Al de cette même gamme b′ pour le réglage à 100 de l'appareil.

Ainsi sont comparées, à des gammes (b ou b′) témoins, où n'intervenaient ni vanadium ni titane, mais des quantités d'aluminium variables d'un terme à l'autre, des gammes (a et a′) contenant vanadium et titane, que l'on a éliminés au cupferron, et les mêmes quantités d'aluminium que les termes homologues des séries témoins (b et b′).

Résultats: les gammes a et b d'une part, sont identiques entre elles et il en est de même des gammes a′ et b′ d'autre part. Le vanadium et le titane ont donc bien été éliminés, et le milieu résultant de la séparation de ces éléments par le cupferron ne perturbe en rien le dosage de l'aluminium au stilbazo.

c) Les gammes suivantes sont faites en introduisant l'aluminium dès le départ, afin de vérifier qu'aucune perte d'aluminium n'intervient dans la séparation au cupferron du vanadium, et du titane.

Dans quatre ampoules à décantation (100), distribuer respectivement: 5-10-15 et 20 ml de liqueur type d'aluminium (1 ml = 25 γ Al), puis successivement: 5 ml de solution de chlorure de vanadyle (1 ml = 0.5 mg de V) (non oxydés au persulfate); 1 ml de solution de trichlorure de titane (1 ml = 5 mg de Ti) (préalablement oxydé par l'eau oxygénée 1 vol. parag. 40-c); 5 ml de solution de sulfate de sodium (100 g/l); 5 ml de liqueur titrée d'acide sulfurique $2N$; de l'eau pour compléter les différences de volumes, d'un essai à l'autre, dues aux volumes variables de liqueur d'aluminium, enfin 5 ml de solution de cupferron (50 g/l). Quatre extractions successives par 10 ml de chloroforme. Les liquides aqueux sont complétés à 100 ml en fioles jaugées.

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Prélever de chacun des termes 10 ml que l'on reçoit respectivement dans 4 fioles jaugées de 100 ml pour les mesures (parag. 38-b).

d) Même série de quatre essais, mais comportant chacun des quantités doubles d'aluminium. Des liquides aqueux, complétés *in fine* à 100 ml, prélever 5 ml (et non 10 ml) pour les mesures colorimétriques (parag. 38-b).

Résultats. Les gammes c et d sont mesurées à l'aide du photomètre déjà réglé au moyen de la gamme témoin b). Les résultats des mesures pour ces gammes c) et d) se confondent avec ceux qu'a donnés la gamme témoin b).

(43) Ainsi, le mode opératoire décrit aux postes c) et d) du précédent paragraphe montre que l'extraction chloroformique du vanadium (IV) et du titane (IV) par le cupferron n'entraîne pas de pertes en aluminium, et que les résultats du dosage de l'aluminium sont exacts; une telle technique est donc justifiée en vue des applications.

Le Tableau II résume des résultats comparatifs, relevés à propos d'aciers calmés à l'aluminium.

TABLEAU II

RÉSULTATS DE DOSAGES COMPARATIFS DE L'ALUMINIUM DANS L'ACIER

1 No. de l'acier	2 V-Ti	3 Direct	4 Spectro
1	0.029	0.039	0.03
2	0.033	0.046	0.032
3	0.018	0.024	0.021
4	0.075	0.094	0.08
5	0.022	0.0255	0.025
6		0.025	0.022
7	0.035	0.03	0.034
8	0.10	0.11	0.10
9	0.027	0.0297	0.027

A remarquer que, dans leur ensemble, les résultats de la colonne 3 (pas de séparation de V-Ti) sont supérieurs à ceux qu'indique la colonne 2 (séparation de V-Ti), qui eux-mêmes suivent assez bien ceux de la colonne 4 (spectrographie); sans doute faut-il voir la cause des résultats, légèrement plus élevés, que donne la méthode directe, dans l'influence d'éléments en petites quantités, tels que le vanadium, qui, non séparés, perturbent la réaction de l'aluminium au stilbazo.

Il est donc conseillé d'employer de préférence la méthode comportant la séparation au cupferron.

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APPENDICE 1

Détermination de l'aluminium dans les aciers calmés (Al $\leq$ 0.1%)

A. *Séparation du vanadium et du titane*

Principe. Après attaque sulfurique, électrolyse sur cathode de mercure; élimination du titane et du vanadium par le cupferron avec extraction au chloroforme. Réaction colorée de l'aluminium, en milieu tamponné et complexé par l'acide ascorbique, au moyen du ,,stilbazo".

Réactifs particuliers

1. Liqueur titrée d'acide sulfurique 2*N*.
2. Solution de cupferron à 50 g/l.
3. Solution d'acide ascorbique à 50 g/l (dissoudre à froid, ou tiède, à préparer extemporanément).
4. Tampon acéto-acétique: 150 ml de solution d'acide acétique *N*/5 (12 ml d'acide acétique par litre), et 150 g d'acetate d'ammonium, par litre.
5. Solution aqueuse de stilbazo à 0.5 g/l.
6. Liqueur d'aluminium. Solution d'alun de potassium $(SO_4)_3Al_2, SO_4K_2, 24 H_2O$ à 44 g par litre. Prélever 10 ml de cette solution, diluer au litre. De cette solution prélever 100 ml, diluer au litre (1 ml = 2.5 γ Al).

Mode opératoire

Prise d'essai: 1 g d'acier.

1. Attaque par 5 ml d'acide sulfurique (1.83) au demi et de l'eau pour modérer l'attaque. Oxyder par quelques gouttes de solution de persulfate d'ammonium (10 g/l). Porter à l'ébullition pour détruire l'excès de persulfate. Diluer à 70 ml environ.
2. Faire passer dans une cellule pour électrolyse sur cathode de mercure, et électrolyser (3 heures, 6 ampères).
L'électrolyse terminée, soutirer le liquide aqueux, laver la cellule, filtrer le liquide.
3. Concentrer le liquide à 25 ml environ, neutraliser par la soude (400 g/l) (papier tournesol) et acidifier immédiatement par 5 ml de liqueur d'acide sulfurique 2*N*(1).
4. Faire passer en ampoule à décantation (100). Ajouter 5 ml de solution de cupferron (50 g/l) (2). Agiter. Ajouter 10 ml de chloroforme, agiter, soutirer la phase chloroformique. Faire encore trois extractions avec 10 ml de chloroforme. Recevoir les liquides aqueux, en les filtrant, en fiole jaugée de 100 ml, compléter à ce volume.
5. Prise d'essai: 10 ml ou 5 ml de ce liquide. La recevoir en fiole jaugée de 100 ml.
6. Ajouter: 10 ml de solution d'acide ascorbique (50 g/l) (3), agiter; 25 ml de tampon 150 ml — 150 g (4), agiter; repos 10 min; 10 ml de réactif stilbazo (0.5 g/l) (5). Agiter. Compléter à 100 ml avec de l'eau.

Gamme d'étalonnage

Prise d'essai 1 g de fer pur.

1 et 2. Attaque et électrolyse sur cathode de mercure (opér. 1 et 2 du mode opératoire).
3. Concentrer et neutraliser (opér. 3).
4. Extraction au cupferron (opér. 4).
5. Prélever cinq prises d'essai 10 ml ou 5 ml (du liquide, ayant subi l'extraction, et complété à 100 ml) que l'on reçoit dans 5 fioles jaugées (100).

Ajouter de la liqueur d'aluminium (1 ml = 2.5 γ Al)[6]:
0 5 10 15 20 ml, contenant:
0 12.5 25 37.5 50 γ Al
correspondance en % d'Al de l'acier, pour prise d'essai 10 ml
0 0.0125 0.025 0.0375 0.05% d'Al
et pour prise d'essai 5 ml:
0 0.025 0.05 0.075 0.1% d'Al
6. Ajouter les réactifs indiqués en opération 6°) ci-dessus.

Mesures photométriques

λ = 515 mμ. Cuves de 2 ou 3 cm. Photométrie différentielle, les cuves étant choisies telles que la densité optique du terme de la gamme exempt d'aluminium soit voisine de 1, et le terme 50 γ Al de cette gamme ne soit pas supérieur à 2. Régler le photomètre* au zéro avec le terme de la gamme exempt d'aluminium, et à 100 avec le terme 50 γ de cette gamme.

Mesurer les densités optiques des termes de la gamme et de l'essai réel.

Calcul. Soit p g Al mesuré à l'aide de la droite d'étalonnage:

$$p \times \frac{100}{10 \text{ ou } 5} \times 100 = \text{Al \% de l'acier.}$$

B. *Cas de l'absence de titane et de vanadium*

Principe. Après attaque sulfurique, électrolyse sur cathode de mercure. Réaction colorée de l'aluminium, en milieu tamponné et complexé par l'acide ascorbique, au moyen du ,,stilbazo''.

Réactifs particuliers

Les précédents du cas A, et en outre:

7. Acide sulfurique dilué: 30 ml de liqueur titrée d'acide sulfurique 2*N* sont complétés à 100 ml en fiole jaugée.

Prélever 10 ml que l'on reçoit en fiole jaugée de 100 ml, compléter à ce volume; cette seconde dilution constitue le réactif.

8. Tampon acéto-acétique: 150 ml de solution d'acide acétique *N*/5 (12 ml d'acide acétique crist. par litre) et 100 g d'acétate d'ammonium, compléter au litre avec de l'eau.

9. Indicateur bleu de bromothymol. Dans un petit erlenmeyer, 0.1 g de bleu de bromothymol est mis en solution dans un peu d'eau (15 ml environ) et 3.2 ml de soude *N*/20; chauffer légèrement. Après dissolution, diluer à 500 ml en fiole jaugée, avec de l'eau.

Mode opératoire

Prise d'essai: 1 g d'acier.

1 et 2. Attaque et électrolyse sur cathode de mercure: opér. 1 et 2 du cas A: présence de vanadium et de titane.

3. Compléter le liquide (filtré) à 100 ml en fiole jaugée. En prélever 5 ml que l'on reçoit en fiole jaugée (100).

A l'aide d'un même volume de 5 ml, titrer par l'ammoniaque (0.9) *au dixième* en présence d'indicateur bromothymol-bleu (9), et déterminer le volume d'ammoniaque au 1/10 nécessaire pour atteindre le virage. Verser ce même volume d'ammoniaque dans la fiole jaugée (100) contenant la prise aliquote de 5 ml. Ajouter immédiatement 5 ml d'acide sulfurique dilué (7), agiter et laisser reposer 10 min environ.

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* Ces indications sont données pour le spectrophotomètre JEAN ET CONSTANT.

4. Ajouter: 10 ml de solution d'acide ascorbique (50 g/l) (3); 25 ml de tampon (150 ml — 100 g) (8) agiter, repos 10 min; 10 ml de réactif stilbazo (0.5 g/l) (5) et compléter à 100 ml avec de l'eau.

Gamme d'étalonnage

Prise d'essai: 1 g de fer pur.

Attaque, électrolyse sur cathode de mercure: opérations 1 et 2 du mode opératoire.

Prélever cinq prises d'essai de 5 ml (du liquide complété à 100 ml). Les neutraliser par l'ammoniaque au dixième selon op. 3, et ajouter 5 ml d'acide sulfurique dilué (7).

Ajouter respectivement de la liqueur d'aluminium (1 ml = 2.5 γ Al) (6):

	0	5	10	15	20 ml
contenant:	0	12.5	25	37.5	50 γ Al
correspondant à:	0	0.025	0.05	0.075	0.1% d'Al de l'acier

Opérer enfin selon oper. 4 du mode opératoire.

Mesures photométriques. Selon le mode opératoire A.

APPENDICE 2

Aciers de nitruration

A. *Cas de la présence de titane* (Al $\leq$ 2%)

Principe. Attaque sulfurique et électrolyse sur cathode de mercure; séparation du titane par l'acide *p*-hydroxyphénylarsinique. Réaction de l'aluminium avec le stilbazo.

Réactifs particuliers

Ceux de l'appendice 1, en outre:

10. Liqueur titrée d'acide sulfurique 4*N*.
11. Solution d'acide *p*-hydroxyphénylarsinique 50 g/l.
12. Tampon acéto-acétique: 150 ml d'acide acétique *N*/5 (12 ml d'acide acétique crist. par litre) et 175 g d'acétate d'ammonium, par litre.

Mode opératoire

Prise d'essai: 0.5 g d'acier.

Attaque et électrolyse sur cathode de mercure: opér. 1 et 2 appendice 1 cas A.

3. Concentrer le liquide électrolysé à 60 ml environ, neutraliser par l'ammoniaque (0.9) *au demi* (papier tournesol).

Ajouter: 15 ml de liqueur titrée d'acide sulfurique 4*N* (10), 20ml de solution d'acide *p*-hydroxyphénylarsinique (50 g/l) (11). Porter rapidement à courte ébullition, refroidir, transvaser en fiole jaugée de 100 ml et compléter à ce volume avec de l'eau. Repos 12 heures. Filtrer (bande bleue Durieux).

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Prélever du filtrat: 5 ml que l'on reçoit en fiole jaugée de 50 ml, compléter à ce volume avec de l'eau.

De ce liquide, prélever 5 ml, que l'on reçoit en fiole jaugée (100).

4. Ajouter: 20 ml de solution d'acide ascorbique (50 g/l) (3); 25 ml de tampon (150-175) (12) agiter; repos 10 min; 10 ml de réactif stilbazo (0.5 g/l) (5) et compléter à 100 ml avec de l'eau.

Gamme d'étalonnage

Prise d'essai: 0.5 g de fer pur.

Opération 1, 2 et 3 ci-dessus.

Aux 5 prises d'essai de 5 ml reçues en fioles jaugées (100), ajouter respectivement, de la liqueur d'aluminium[6] (1 ml = 2.5 γ Al)

0 5 10 15 20 ml

contenant:

0 12.5 25 37.5 50 γ Al

correspondant à:

0 0.5 1 1.5 2% d'Al de l'acier

Mesures photométriques, selon le mode opératoire appendice 1-A.

B. *Absence de titane*; Al $\leq$ 1.25%

Principe. Attaque du métal. Neutralisation et réaction de l'aluminium au stilbazo.

Mode opératoire

Prise d'essai: 0.04 g.

1. Attaque par 5 ml d'acide sulfurique (1.83) *au demi.* Porter à l'ébullition. Compléter à 100 ml avec de l'eau en fiole jaugée.

Filtrer (filtre Durieux bande blanche).

Prélever de ce liquide 10 ml que l'on reçoit en fiole jaugée (100).

2. Un prélèvement de 10 ml du même liquide est neutralisé par l'ammoniaque (0.9) *au dixième* en présence de bleu de bromothymol (9). Mesurer le volume d'ammoniaque au 1/10 nécessaire. Ajouter, dans la fiole jaugée (100) le même volume d'ammoniaque au dixième ainsi déterminé au préalable.

Ajouter immédiatement: 5 ml d'acide sulfurique dilué (7), agiter, repos 10 min.

3. Ajouter: 20 ml de solution d'acide ascorbique (50 g/l) (3), 25 ml de tampon (150 ml — 175 g) (12); agiter, repos 10 min; 10 ml de réactif stilbazo (0.5 g/l) (5) et de l'eau pour compléter à 100 ml.

Gamme d'étalonnage

Attaquer 0.04 g de fer pur et opérer selon opér. 1 et 2 ci-dessus (jusqu'à la neutralisation et l'addition de l'acide sulfurique dilué (7), tout en faisant 5 prélèvements de 5 ml (et non un seul). A chacun d'eux, ajouter respectivement:

liqueur d'aluminium (1 ml = 2.5 γ Al(6)):

0 5 10 15 20 ml

contenant:

0 12.5 25 37.5 50 γ Al

correspondant à:

0 0.3125 0.9375 1.25% d'Al de l'acier

Réaction colorée selon opér. 3 ci-dessus.

Mesures photométriques. Selon le mode opératoire de l'appendice 1-A.

APPENDICE 3

Aciers à aimants (Al $\leq$ 15%)

Principe. Celui de: appendice 2 B.

Mode opératoire

Prise d'essai: 0.0335 g.

1. Attaque par 5 ml d'acide sulfurique (1.83) *au demi.* Porter à l'ébullition. Compléter à 500 ml en fiole jaugée. Prélever 5 ml de ce liquide que l'on reçoit en fiole jaugée (100).

2. Un prélèvement de 5 ml de ce même liquide est neutralisé par l'ammoniaque (0.9) *au dixième* en présence de bleu de bromothymol (9).
Mesurer le volume nécessaire d'ammoniaque au dixième. Ajouter dans la fiole jaugée (100), le même volume d'ammoniaque au dixième ainsi déterminé au préalable. Ajouter immédiatement 5 ml d'acide sulfurique dilué (7), agiter, repos 10 min.

3. Ajouter 20 ml de solution d'acide ascorbique (50 g/l) (3) 25 ml de tampon (150 ml-175 g) (12), agiter, repos 10 min; 10 ml de réactif stilbazo (0.5 g/l) (5) et de l'eau pour compléter à 100 ml.

Gamme d'étalonnage

Attaquer 0.0335 g de fer pur et opérer selon opér. 1 et 2 ci-dessus (jusqu'à la neutralisation et l'addition de dilution sulfurique (7), tout en faisant 5 prélèvements de 5 ml (et non un seul). A chacun d'eux, ajouter respectivement:

liqueur d'aluminium (1 ml = 2.5 γ) (6)

0 5 10 15 20 ml

contenant:

0 12.5 25 37.5 50 γ Al

correspondant à:

0 3.75 7.5 11.25 15% d'Al

Réaction colorée selon opér. 3 ci-dessus.

Mesures photométriques, selon le mode opératoire de l'appendice 1-A.

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RÉSUMÉ

Le dosage colorimétrique de l'aluminium, au moyen d'un réactif nouvellement indiqué, le ,,stilbazo", est étudié.

On aboutit à une méthode de détermination directe dans les aciers alliés à l'aluminium: aciers de nitruration, aciers à aimants.

L'aluminium de calmage est dosé par une technique comportant l'électrolyse sur cathode de mercure, la séparation du titane et du vanadium éventuels par extraction chloroformique des complexes de ces éléments avec le cupferron et le dosage colorimétrique final.

Au cours de ces recherches expérimentales, des observations ont été faites concernant l'influence de nombreux éléments sur la réaction de l'aluminium avec le stilbazo. Les réactions du vanadium avec différents réactifs (dicyandiamidine, diantipyrylphénylméthane, α-benzoïnoxime) ont été étudiées. Enfin le complexe silico-vanado-tungstique a également été étudié au cours de ce travail.

SUMMARY

Colorimetric determination of aluminium by means of a new reagent, stilbazo, is studied.

The investigation leads to a method for the direct determination of aluminium-steel alloys: nitrided steels, magnetic steels.

The aluminium is determined by a technique consisting of electrolysis with mercury cathode, separation of titanium and vanadium, if present, by chloroform extraction of the complexes of these elements with cupferron, and, finally, colorimetric determination.

During these experimental investigations, observations have been made concerning the influence of a number of elements on the reaction of aluminium with stilbazo. The reactions of vanadium with various reagents (dicyandiamidine, diantipyrylphenylmethane, α-benzoinoxime) and the silico-vanado-tungstic complex have been studied.

ZUSAMMENFASSUNG

Die kolorimetrische Bestimmung von Aluminium mit Hilfe eines neuentwickelten, Reagenz, dem ,,Stilbazo" wurde studiert.

Die Untersuchungen führten zu einer direkten Bestimmungsmethode in Aluminium enthaltenden Stählen, wie Nitrier- und Magnetstählen.

Aluminium wird nach einer Methode bestimmt, die aus einer Elektrolyse an Quecksilberkathoden, Abtrennung von evtl. vorhandenen Titan und Vanadium durch Extraktion der Cupferronkomplexe dieser Elemente mit Chloroform und schliesslich der kolorimetrischen Bestimmung besteht.

Im Laufe der experimentellen Untersuchungen wurde der Einfluss, den zahlreichen Elementen auf die Reaktion des Aluminiums mit Stilbazo ausüben, beobachtet. Die Reaktion des Vanadiums mit verschiedenen Reagenzien (Dicyandiamidin, Diantipyrylphenylmethan, α-Benzoinoxim) wurde untersucht. Schliesslich wurde im Lauf dieser Arbeit zugleich der Silizium-Vanadium-Wolframkomplex untersucht.

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DIE MIKROPHOTOMETRISCHE BESTIMMUNG VON KOBALT IM BLUTSERUM UND ANDEREN BIOLOGISCHEN SUBSTANZEN

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Der Bedarf an Kobalt für Tier und Mensch ist im Vergleich zu anderen bis heute als lebensnotwendig erkannten Spurenelementen ausserordentlich gering. Der Kobaltgehalt des Blutserums und verschiedener Organe ist daher sehr niedrig und seine mikroanalytische Erfassung bereitet grosse Schwierigkeiten. Soweit es sich um pflanzliche oder tierische Probesubstanzen handelt, die in der Regel in grösseren Mengen zur Verfügung stehen, gelingt die Bestimmung von Kobalt nach einer Anreicherung aus einer grösseren Ausgangsmenge. Dies ist aber a.B. bei laufenden Untersuchungen des Serumkobaltspiegels am Patienten selbst nicht möglich.

Da im Blutserum etwa 0.1 bis 1.5 $\gamma\%$ Kobalt enthalten sind und für laufende Untersuchungen möglichst nur wenige Milliliter Serum für eine Bestimmung benötigt werden sollen, ist hierfür eine Mikromethode, welche die exakte Bestimmung von Hundertstel Mikrogramm Kobalt ermöglicht, eine unbedingte Voraussetzung.

In der neueren Literatur sind zahlreiche kolorimetrische bezw. photometrische Kobaltbestimmungsmethoden enthalten, die sich vorwiegend der Reaktionen mit Rhodanionen im heterogenen Lösungsmedium[1,2,3] oder mit Nitroso-R-Salz[2,4 bis 16], ferner Nitrosophenol[17], Dimethylglyoxim und Benzidin[18], Isonitrosodimedon[19], Diäthyldithiocarbamat[22,21] und anderen bedienen. Die Bestimmung mit den empfindlicheren unter diesen Methoden erfordert aber eine Ausgangsmenge von etwa 50 bis 100 ml Serum, die für die erwähnten Untersuchungen viel zu gross ist.

Wolff[22] gelang es unter Verwendung von 25 ml Serum auf spektrographischem Wege im kurzwelligen Teil des sichtbaren Spektrums Kobaltgehalte von 0.17 bis 1.48 $\gamma\%$ mit einer Streuung von $\pm 25\%$ festzustellen. Dies stellt einen wesentlichen Fortschritt dar, wenn die benötigte Serummenge auch noch immer relativ gross und die Genauigkeit der Methode nicht sehr befriedigend sind.

Literatur S. 561.

Die Wahl der Bestimmungsreaktion

Für die Entwicklung einer exakten und hinreichend empfindlichen Mikromethode erschien uns nach Prüfung der Möglichkeiten, die die Spektrographie, Polarographie und objektive Photometrie für die Kobaltbestimmung gewähren, die letztere Methode als aussichtsreichster Weg.

Von den oben genannten Farbreaktionen zur photometrischen Bestimmung von Kobalt ist jene mit Nitroso-R-Salz am geeignetsten. Der wasserlösliche Kobaltkomplex des Nitroso-R-Salzes (1-Nitroso-2-Naphthol-3,6-disulfosaures Natrium) ist rot und in seiner Empfindlichkeit (0.02 γ/ml) und Spezifität den anderen Reagenzien überlegen. Unter den gleichen Reaktionsbedingungen bilden Eisen einen grünen und Kupfer einen orangegelben Komplex, welche von verdünnter Salpetersäure in der Hitze zerstört werden, während der Kobaltkomplex beständig ist. Bei grösseren Mengen Eisen und Kupfer ist jedoch eine Trennung notwendig.

Auf Grund der Empfindlichkeit dieser Reaktion müssten für die photometrische Bestimmung von Kobalt 5 bis 10 ml Blutserum genügen, wenn es gelingt:

1) Mit Hilfe einer geeigneten Trennungsoperation störende Mengen Eisen und Kupfer, welche im ungünstigsten Falle in 100- bis 10,000-facher Menge des Kobaltgehaltes (z.B. im Gesamtblut) vorhanden sein können, ohne Verluste an Kobalt zu entfernen,

2) Kobalt quantitativ zu isolieren und in einem maximalen Lösungsvolumen von 1 ml spektrophotometrisch zu bestimmen.

Das Entfernen von Eisen und Kupfer

Nach Angaben von TROITSKAJA[6] stören Eisen und Kupfer die Bestimmung von Kobalt mit Nitroso-R-Salz nicht, wenn deren Verhältnis 500:20:1 nicht überschreitet. HALL UND YOUNG[12] machen ähnliche Angaben. Beim Blutserum werden diese Mengenverhältnisse von Kupfer weit überschritten und bei fast allen biologischen Substanzen auch von Eisen. Für die Trennung dieser beiden Elemente von Kobalt kommt zur Vermeidung von Verlusten durch Oberflächeneffekte nur eine Ausschüttelungsreaktion in Frage. Aus der Literatur und aus eigenen Untersuchungen über die Extraktion mit verschiedenen organischen Reagenzien ergeben sich für diese Trennung die in Tabelle I angeführten Möglichkeiten, deren Eignung näher untersucht wurde.

Nach Berücksichtigung der Bedingungen, denen diese Trennung entsprechen sollte, ergab sich der folgende vorteilhafteste Weg: Extraktion von Kupfer und Eisen bei pH 2.5 mit Dithizon und Oxin nacheinander oder in Mischung[24] und anschliessende Extraktion von Kobalt bei pH 5 mit Natriumdiäthyldithiocarbamat und Chloroform.

Literatur S. 561.

TABELLE I

DIE TRENNUNG DES KOBALTS VON EISEN UND KUPFER DURCH EXTRAKTION

Reagenz und Solvent	pH	die organische Phase enthält	die wässr. Phase enthält	Literatur
Salzsäure-Äther	6.5NHCl	Fe III	Co, Cu, Fe II	14,23
Kupferron-$CHCl_3$	0	Fe III, Cu	Co	23
Rhodan-Aceton	3	Co, Fe III, Cu II	Fe II, Cu I	2,3
Nitrosophenol-Petroläther	6 — 7	Co, Fe III	Fe II, Ni, Cu	17
Oxin-$CHCl_3$	2.5	Cu, Fe III	Co	23
1-Nitroso-2-Naphthol $CHCl_3$	3 — 4	Cu, Co	Fe	25
Dithizon-$CHCl_3$	8 — 9	Fe II, Cu, Co	Fe III	25
Dithizon-$CHCl_3$	2	Cu	Fe, Co	25
Thionalid-$CHCl_3$	6 — 7	Fe II, Co	Cu	23

Diese Art der Trennung hat gegenüber den oben angeführten einige Vorteile.

1) Sowohl Kobalt als auch Kupfer und Eisen liegen getrennt von den Ballastelementen in einzelnen Chloroformphasen vor und jedes Element kann, falls gewünscht, für sich einer Bestimmung zugeführt werden.

2) Die extrem geringe Menge von 0.02 γ Co wird verlustlos extrahiert, da seine Komplexe mit Carbamat und Oxin beim angegebenen pH-Wert hohe Stabilität und sehr günstige Extraktionskoeffizienten haben und ferner von gleichzeitig extrahierten geringen Mengen Mangan, Blei, Nickel und Zink „mitgenommen" werden. Oxin ist an der Extraktion beteiligt, da fast der gesamte Oxinüberschuß von der Eisenextraktion bei pH 2.5 in der wässrigen Phase verbleibt (Oxin ist von pH 5 bis 9 chloroformextrahierbar[26]) und dann beim höheren pH als Oxinat oder freies Oxin zur Extraktion gelangt.

3) Ein eventueller hoher Phosphatgehalt des Probematerials stört bei den niedrigen pH-Werten der Extraktionen noch nicht.

Die Bildung des Farbkomplexes und Messung seiner Absorption

Das im Chloroformextrakt enthaltene Kobalt ist nach dem Zerstören der organischen Substanz mit Mineralsäuren in den Nitroso-R-Salzkomplex zu überführen. Nach OVENSTON[13] hat der pH-Wert der Lösung auf die Reaktionsgeschwindigkeit der Bildung dieses Komplexes wesentlichen Einfluss. Optimale Bedingungen liegen von pH 5 aufwärts vor. Zur Einstellung des günstigen pH-Wertes verwendeten wir daher einen Natriumacetatpuffer vom pH 6.

Da das Reagenz in wässriger Lösung eine gelbe Färbung aufweist, liegt zur Photometrierung stets ein Gemisch des Farbkomplexes mit dem Reagenzüberschuß vor, wobei die Absorptionsmaxima von Reagenz und Kobaltkomplex bei 420 mμ zusammenfallen[13].

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Entgegen anderen Angaben[7] ist für die Messung eine Filterung zwischen 500 und 520 mμ am geeignetsten, da hier die Reagenzabsorption bereits sehr gering, dagegen die Komplexabsorption noch hinreichend gross sind.

Als Photometer verwendeten wir zunächst das Mikrophotometer von KRUMHOLZ[28], das mit 2 cm-Küvetten von 1 ml Inhalt ausgerüstet ist. Das dem Photometer zugehörige Grünfilter erwies sich als geeignet. Im Laufe der Versuche mit diesem Photometer zeigte es sich, dass die Messung der Extinktionen von Kobaltmengen unter 0.05 γ mit der vorhandenen Schichtdicke nicht mit befriedigender Genauigkeit möglich war. Wir verwendeten daher für die weiteren Untersuchungen ein im Institut hergestelltes Mikrophotometer mit Kapillarküvetten[32], die bei einer Schichtdicke von 10 cm ein Lumen von 3 mm hatten, was einem Volumen von 0.7 ml entspricht. Dieses Einzellen-Mikrophotometer ist mit einer Lange-Selenzelle und einer Lichtquelle von 6 Volt und 30 Watt, die durch einen Stabilisator nach KAHOVEC-TREIBER[27] konstant gehalten wird, ausgerüstet. Die Lichtstrahlen werden durch ein Linsensystem gebündelt, durch eine Blende begrenzt und durch die Kapillare geschickt. Zur Messung des Photostroms (Ausschlagsmethode) diente das Multiflexgalvanometer MG 2 mit regelbaremVorschaltwiderstand. Die dickwandigen kalibrierten Kapillaren sind an beiden Enden plangeschliffen und werden ähnlich den Polarimeterröhrchen mittels Glasplättchen und Schraubkappen verschlossen. Eine blasenfreie Füllung erfolgt leicht durch Verwendung eines zu einer Kapillare ausgezogenen Glasröhrchens, welches bis zum Boden der Kapillarküvette reichen muss. Als Filter wurde das dem KRUMHOLZphotometer beigegebene Grünfilter verwendet. Die Messgenauigkeit dieses Photometers liegt bei etwa ±0.5%. Für die Messung ist natürlich jedes Photometer mit Kapillarküvetten ähnlicher Abmessungen brauchbar.

Die Ausführung der Kobaltbestimmung

Nach Feststellung der geeigneten Reagenzkonzentration und der erforderlichen Reagenzmenge ergab sich die folgende Arbeitsweise:

Reagenzien: Mischsäure (Schwefelsäure und Salpetersäure 1 : 1), Perchlorsäure p.a., *M*/10 Salzsäure, Ammoniak verd., Thymolblaulösung, *o*-Oxychinolin 1%ig in $CHCl_3$, Dithizon 0.02%ig in $CHCl_3$, Ammoniumtartratlösung 10%ig, Natriumdiäthyldithiocarbamat 2%ige wässrige Lösung, Natriumnitrat 10%ig, Natriumacetat 10%ig, Nitroso-R-Salzlösung 0.05%ig, Salpetersäure 70%ig, Chloroform p.a., Wasserstoffperoxyd 30%ig.

10 ml Blutserum werden mit 5 ml Mischsäure und 10 ml Perchlorsäure in einem Quarzkolben bis zur farblosen Lösung erhitzt und hierauf auf dem Sandbad bis zum vollständigen Abrauchen der Mineralsäuren belassen.

Den Rückstand löst man (eventuell unter Erwärmen) mit insgesamt 50 ml *N*/10 Salzsäure und überführt in einen 100-ml Schütteltrichter. Nach Zusatz einiger

Tropfen Thymolblauindikatorlösung bringt man durch Zutropfen von verdünntem Ammoniak auf pH 2.5 (orangegelbe Farbe). Zweckmässig stellt man sich eine Vergleichsfarbe mit Salzsäure-Kaliumbiphtalatpuffer vom pH 2.5 her. Nun schüttelt man das Kupfer mit 10 ml Dithizonlösung 5 Minuten lang aus und schüttelt mit 10 ml Chloroform nach Ablassen der Dithizon-Chloroformphase nochmals nach. Nach Zusatz eines Tropfens Wasserstoffperoxyd schüttelt man das Eisen mit 10 ml Oxinlösung 2 Minutenlang aus und lässt die Chloroformphase ab. Hierauf extrahiert man mit je 10 ml Chloroform noch zwei bis drei Mal und vereinigt die Extrakte. (Wird auf die getrennte Erfassung von Eisen und Kupfer kein Wert gelegt, so setzt man zur Extraktion der beiden je 10 ml Dithizonlösung und Oxinlösung auf einmal zu und schüttelt dreimal mit je 10 ml Chloroform nach.) Die Extrakte können nach Vertreiben des Chloroforms und Mineralisieren mit Mischsäure und Perchlorsäure zur Bestimmung von Eisen und Kupfer verwendet werden.

Zur Lösung im Schüttelrichter fügt man nun 3 ml Ammoniumtartratlösung und stellt mit verdünntem Ammoniak auf etwa pH 5 ein (Tüpfeln auf Indikatorpapier). Nach Zusatz von 5 ml 2%iger Diäthyldithiocarbamatlösung extrahiert man 3 mal mit je 10 ml Chloroform. Diese Extrakte engt man durch Abdestillieren des Chloroforms auf wenige ml ein und dampft diese nun nach und nach in einem Quarzspitzröhrchen unter einem Oberflächenverdampfer aus Quarz zur Trockene ein. Ein Erhitzen von unten ist hierbei nicht vorteilhaft, da Verluste durch Verspritzen und Klettern der Lösung auftreten.

Zum Rückstand der metallorganischen Komplexe im Spitzröhrchen setzt man nun 0.2 ml Natriumnitratlösung als Spurenträger und 0.25 ml Mischsäure und 1 ml Perchlorsäure zum Mineralisieren der Komplexe zu und erhitzt im Universalheizkörper nach GORBACH[29] oder auf dem Sandbad, indem man den Schliffstopfen des Quarzspitzröhrchens verkehrt als Rückflusskühler aufsetzt. Nachdem sich die Lösung vollständig entfärbt hat, entfernt man den Stopfen und raucht die Säuren ab. Die letzten Reste Schwefelsäure vertreibt man über einer Mikroflamme.

Zum Trockenrückstand fügt man nun 0.5 ml Acetatpuffer und 0.2 ml Nitroso-R-Salzlösung und taucht das Spitzröhrchen zum Entwickeln des Kobaltkomplexes genau 1 Minute lang bis zur Hälfte in ein kräftig siedendes Wasserbad ein. Nun setzt man 0.2 ml 70%ige Salpetersäure zu und taucht in gleicher Weise 1 Minute in das siedende Wasserbad, worauf man gleich in ein kaltes Wasserbad zum Abkühlen setzt. Nach dem Abkühlen füllt man mit Hilfe einer 1 ml-Nullpunktpipette, die mit einer Saugvorrichtung versehen ist[30] mit bidestilliertem Wasser auf 1 ml auf, spritzt in ein Zentrifugiergläschen und zentrifugiert die von Blei- und Bariumsulfat herrührende geringe Trübung ab (Pb aus dem Serum und Schwefelsäure, Pb und Ba aus Perchlorsäure). Nun füllt man wie oben beschrieben die Kapillarküvette und misst die Absorption bei 520 mμ ($= I$). Zur Einstellung des vollen Galvanometerausschlages ($= I_0$) verwendet man eine

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mit Acetatepuffer und Reagenzlösung in gleicher Weise wie oben versetzte und behandelte Lösung. Die Extinktion errechnet sich wie üblich $E = \log I_0/I$.

Die Eichkurve (Fig. 1) wird ermittelt, indem man je 20 mg Natriumnitrat (= 0.2 ml der Natriumnitratlösung) mit Zusätzen von 0.02; 0.05; 0.1; 0.2 und 0.3 γ Kobalt in der gleichen Weise behandelt, wie zuvor beschrieben. Der Kobaltzusatz erfolgt mit der Membranbürette nach GORBACH[31].

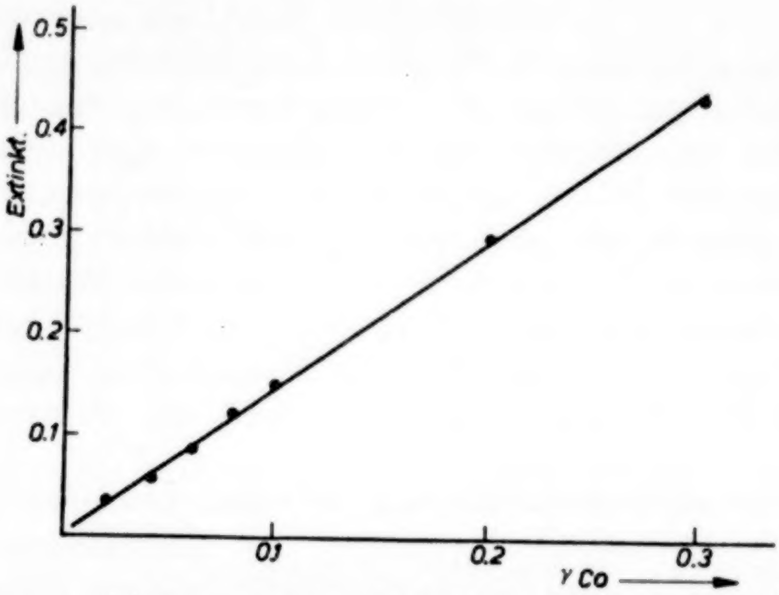

Fig. 1. Bestimmung von Kobalt mit Nitroso-R-Salz. Grünfilter, Kapillarküvetten mit 10 cm Schichtdicke.

Die Ermittlung des Blindwertes (Kobaltgehalt der Reagenzien) erfolgt parallel zur Serumanalyse nach der gleichen Vorschrift, jedoch mit 5fachen Reagenzmengen. Die hierbei erhaltene Extinktion (geteilt durch 5) wird jeweils von der Serumkobaltextinktion abgezogen. Wir ermittelten Blindwerte von etwa 0.01 γ/Co für die in der Vorschrift genannten Reagenzmengen.

TABELLE II

BELEGANALYSEN, DURCHGEFÜHRT MIT 10 ml BLUTSERUM EINER KUH (8-JÄHRIG) MIT EINEM SERUMKOBALTGEHALT VON 0.059 γ (= 0.59 γ %).

γ Co zugegeben	γ Co wiedergefunden	Δ γ Co
0.000	0.063	+0.004
0.020	0.085	+0.006
0.040	0.095	—0.004
0.060	0.120	+0.001
0.080	0.133	—0.006
0.100	0.164	+0.005

Trotz des behelfsmässigen Aufbaues unserer Messeinrichtung betrug der relative Fehler bei unseren Bestimmungen selten mehr als ±5%.

Nach der angegebenen Arbeitsvorschrift können sämtliche biologischen Substanzen auf Kobalt untersucht werden. Die Einwaage ist stets so gross zu halten, dass die zu erwartende Kobaltmenge zwischen 0.02 und 0.3 γ liegt.

Bemerkungen zur Methode

Besondere Beachtung verdient die vollständige Zerstörung der organischen Substanzen im Rückstand der Kobalt-Chloroformextrakte. Verbleibt hier ein geringe Gelbbraunfärbung (erkenntlich nach Zusatz des Acetatpuffers), so liegt die Absorption dieser Färbung im Messbereich der Methode und verursacht hohe Plusfehler. In der Regel gelingt die völlige Zerstörung mit den angegebenen Säuremengen. Mit Salpetersäure und Perchlorsäure allein gelingt die völlige Entfärbung vermutlich infolge der niedrigeren Siedetemperatur jedoch nicht.

Die Methode erfordert sehr gewissenhaftes und sauberes Arbeiten und liefert bei genauer Einhaltung der Vorschrift sehr zuverlässige Werte. Die Reinigung der Glas- und Quarzgeräte und Gefässe erfolgt am besten mit Seifenlösung, Kochen in Salzsäure (1:1) und bidestilliertem Wasser. Als Reagenzien verwendet man am besten Mercks p.a. Reagenzien, welche die niedrigsten Blindwerte zeigten.

Zuletzt möchten wir darauf hinweisen, dass man beim Erhitzen der Quarzspitzröhrchen im Universalheizkörperstativ und darauffolgendem Abkühlenlassen diese hierbei auf keinem Fall im Heizkörper belassen darf. Beim Erhitzen erweitern sich die Bohrungen infolge thermischer Ausdehnung des Aluminiums, die Spitzröhrchen aus Quarz sinken tiefer in die Form und werden beim darauffolgenden Abkühlen und Zusammenziehen des Aluminiums zerdrückt!

Für die Unterstützung unserer Arbeit sind wir dem Vorstand des Institutes Herrn Prof. Dr. G. Gorbach zu Dank verpflichtet.

ZUSAMMENFASSUNG

Die photometrische Bestimmung von Kobalt erfolgt als Nitroso-R-Salz-Komplex in 5—10 ml Blutserum. Die organische Substanz wird mit Mineralsäuren zerstört. Eisen und Kupfer werden mit Oxin und Dithizon entfernt und können gesondert einer Bestimmung zugeführt werden. Kobalt wird mit anderen Spurenelementen als Diäthyldithiocarbamat bezw. Oxin-Komplex mit Chloroform ausgeschüttelt und hierauf in den Nitroso-R-Salzkomplex übergeführt. Die photometrische Messung erfolgt mit Kapillarküvetten von 10 cm Länge und 0.7 ml Inhalt unter Verwendung eines Grünfilters. Mengen von 0.02 bis 0.3 γ Kobalt können mit einem Fehler von $\pm 5\%$ quantitativ bestimmt werden.

SUMMARY

A photometric method is proposed for the determination of cobalt in the form the nitroso-R-salt complex in 5—10 ml of blood serum. The organic matter is destroyed by mineral acids. Iron and copper are separated by oxine and dithizone; they can be determined later. Cobalt (just like traces of other elements), complexed by diethyldithiocarbamate and oxine, is extracted by chloroform and then determined in the form of the nitroso-R-salt complex. The photometric measurement is carried out in a capillary cuvette 10 cm long and 0.7 ml volume, using a green

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filter. Amounts of 0.02—0.3 γ cobalt can be determined quantitatively, with an accuracy of ± 5%.

RÉSUMÉ

Les auteurs proposent une méthode photométrique pour le dosage du cobalt, complexé par le sel de nitroso-R, dans 5 à 10 ml de sérum sanguin. La matière organique est détruite avec des acides minéraux. Le fer et le cuivre sont séparés par l'oxine et la dithizone; ils peuvent ensuite être dosés. Le cobalt (de même que des traces d'autres éléments), complexé par le diéthyldithiocarbamate et l'oxine' est extrait par le chloroforme, puis dosé sous forme du complexe avec le sel de nitroso - R. La mesure photométrique s'effectue avec une cuve capillaire de 10 cm de longueur et 0.7 ml de volume, et un filtre vert. Des teneurs de 0.02 à 0.3 γ de cobalt peuvent être déterminées quantitativement, avec une précision de ± 5%.

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SPECTROPHOTOMETRIC STUDY OF THE FORMALDEHYDE-LEUCO-METHYLENE BLUE REACTION

by

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Methylene blue is known to form a leuco-base on reduction, but the stability of the latter against oxidation by air or oxygen appears to vary with the reducing agents used. Possibly the stability is caused by an association of the base with certain groups derived from the reducing agents themselves. That such is the case with the leuco-base obtained by reduction of methylene blue with HCl and $Na_2S_2O_3$ has been suggested by MATIN AND POPESCO[1], who are also the authors of the method of reduction itself. The possible stabilising group in this particular instance is — $S.SO_3H$, which maintains the leuco-base up to 12 hours even in the presence of atmospheric air. We have considered it expedient to accept this suggestion as a working hypothesis.

LANG[2] observed that formaldehyde turns the leuco-base blue and also suggested the use of the latter as a reagent for detecting formaldehyde, but, as LANG also noted, the test is far from sensitive. This reaction is apparently the reverse of what one expects, but it is to be pointed out that formaldehyde is incapable of turning the leuco-base blue in the absence of air or oxygen. It is thus obvious that formaldehyde only hastens the reaction with oxygen, which is normally held up, in this particular case for about 12 hours, owing possibly to the presence of the stabilising group — $S.SO_3H$.

The colour characteristics of this oxidised compound does not seem to have been systematically studied. The authors have used the spectrophotometric measurements for this purpose and have also observed the effect of sensitising substances on this reaction. In this connection the work of TOBIE[3] on Schiff's reagent, although not quite analogous, has been very suggestive.

EXPERIMENTAL

The leuco-base was prepared according to MATIN[1] by the reduction of methylene blue (Merck, recrystallised) with $Na_2S_2O_3$ and HCl. For every 15 ml of 3.125*M* methylene blue solution were added 3 ml of 0.1*N* HCl and 0.1 ml of 0.097*N*

$Na_2S_2O_3$. The mixture on being kept in the dark for 2 hours becomes colourless. The thiosulphate used in the above is just about the minimum necessary to cause decolorisation.

All the chemicals used were of reagent quality.

The blue colour developed on adding formaldehyde to the leuco-base in the presence of air or oxygen was spectrophotometrically analysed over the entire wavelength (480 — 800 mμ) by means of the Beckman Quartz Spectrophotometer. Only one absorption maximum is shown at 656.5 mμ which is exactly the same as that of pure methylene blue solution[4].

The following factors determining the sensitivity of the blue colour developed in the above manner were studied.

(i) *The dependence of absorption maximum on the content of thiosulphate*

The leuco-base, as already pointed out, is stabilised by the — $S.SO_3H$ group against oxidation. The content of thiosulphate is, therefore, likely to influence the development of the blue colour. In fact the results given in Table I will show that the maximum sensitivity is obtained with the solution of the leuco-base containing the minimum amount of $Na_2S_2O_3$ used for reduction. For the purpose of these experiments increasing amounts of $Na_2S_2O_3$ were added while preparing the leuco-base. The maximum absorption and the approximate time required to attain it, under the circumstances, by the addition of formaldehyde are noted in each case.

(ii) *Effects of sensitising substances*

Preliminary experiments have shown that substances like acetone, ethyl alcohol, diethyl ketone, methyl ethyl ketone increase the sensitivity of the reaction in so far as the colour is intensified, although the wavelength of absorption maximum is not altered at all. Similar sensitisation by alcohols and ketones was observed by Tobie[3] and Hoffpauir *et al.*[5], in their work on Schiff's reagent.

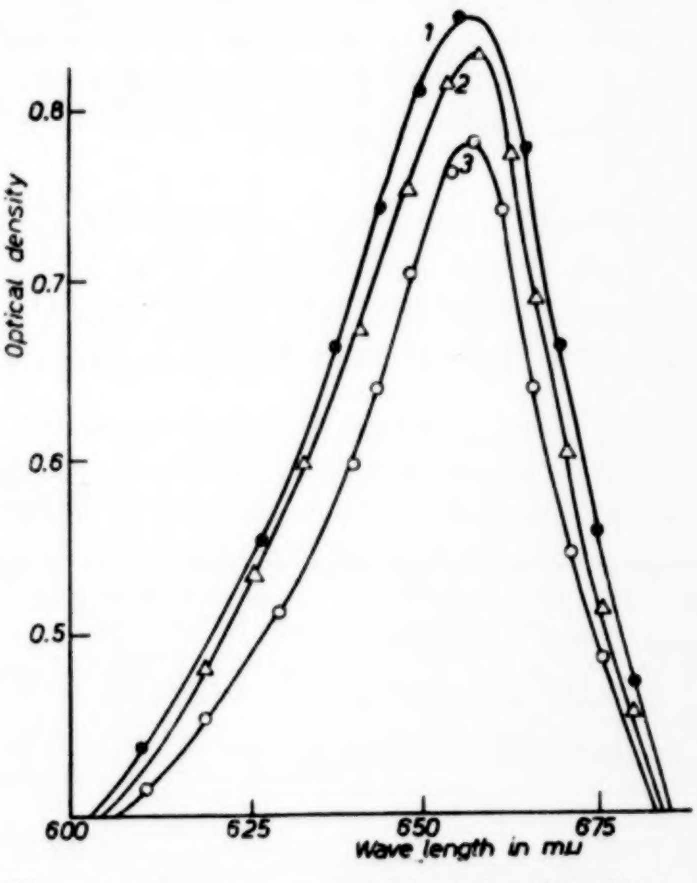

Fig. 1. Curve 1 — sensitised by Me_2CO
Curve 2 — sensitised by EtOH
Curve 3 — without sensitiser

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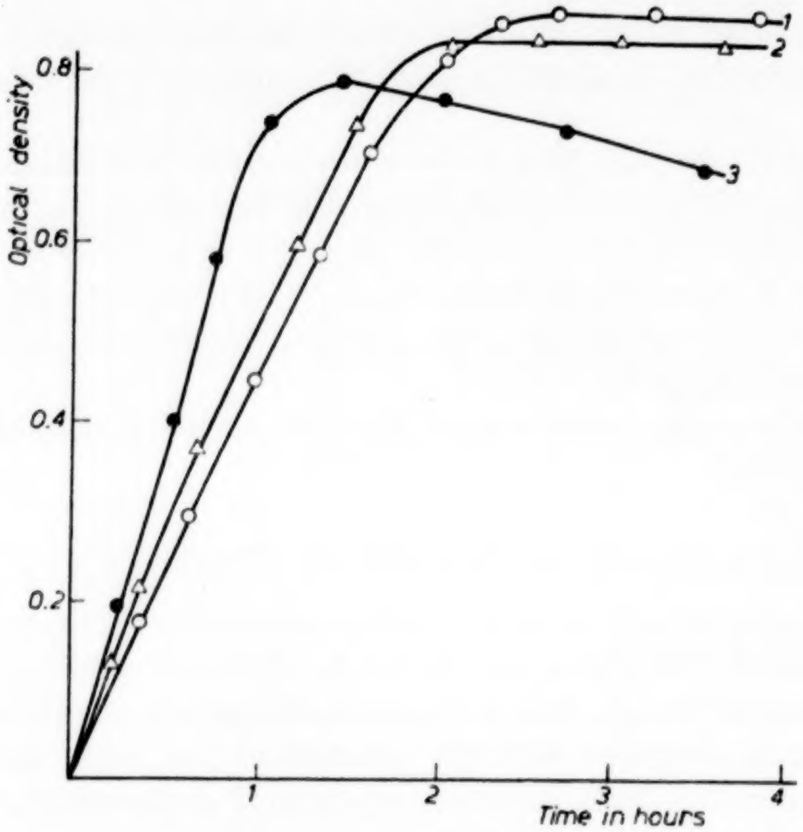

Fig. 2. Curve 1 — sensitised by Me_2CO
Curve 2 — sensitised by EtOH
Curve 3 — without sensitiser
0.45 mg CH_2O per 4 ml leuco-MB
of 3.125*M* conc.

The results obtained by using ethyl alcohol and acetone under otherwise similar conditions are borne out by the graphs shown in Figs. 1 and 2.

Fig. 1 shows that the wavelength corresponding to the absorption maximum is identical in the presence as well as absence of ethyl alcohol and acetone, but the optical density is highest with acetone followed bij that of ethyl alcohol so that the blue colour is deepest in presence of acetone. On the other hand, the times necessary to attain the maximum colour showed a reverse order, *i.e.* the conversion is slowest with acetone and fastest in absence of any sensitising substance, as revealed in the Fig. 2. Methyl alcohol is without any sensitising action.

Further experiments with 4 ml of leuco-base solution to which increasing amounts of acetone were added, show that the sensitivity increases up to about 0.1 ml acetone but not beyond as given in Table II

TABLE I

ml of 0.097*N* $Na_2S_2O_3$ added to 15 ml of 3.125*M* methylene blue	Amount in mg of HCHO per 4 ml of leuco solution	Maximum optical density	Approx. time in hours to attain max. density
0.3	0.45	0.421	7—8
0.15	0.45	0.655	4—4½
0.1	0.45	0.780	1—1¼

TABLE II

EFFECT OF INCREASING AMOUNTS OF ACETONE PER 4 ml OF LEUCO-METHYLENE BLUE CONTAINING 0.45 mg OF HCHO

Acetone in ml	0	0.025	0.050	0.075	0.1	0.125
Max. opt. density	0.780	0.804	0.829	0.852	0.854	0.854

DISCUSSION

The following points emerge from the above results.

Formaldehyde, which is normally capable of reducing methylene blue to the leuco-base[6], helps oxidation of the latter by air or oxygen. In the absence of oxygen formaldehyde is without any effect. Again, in absence of formaldehyde the leuco-base as prepared by reduction with $Na_2S_2O_3$ and HCl is stabilised by an — S. SO_3H group for about 12 hours against oxidation by air or oxygen. Obviously, formaldehyde reacts with the stabilising group thus undoing the effect of the latter. That the leuco-base does not form any complex compound with formaldehyde, as it has been shown to be the case with Schiff's reagent[7], is demonstrated by the fact that the coloured compound has always the absorption maximum at wavelength 656.5 mμ, exactly corresponding to that of methylene blue itself. Moreover, stabilisation against oxidation, even in presence of formaldehyde, is increased in presence of a large concentration of thiosulphate, which supplies the necessary stabilising group.

The exact function of the sensitizers, like acetone and ethyl alcohol, is not clear, but it is shown that they serve a two-fold purpose: they deepen the colour, *i.e.* absorption maximum and at the same time stabilise the maximum; further, the colour development is rendered slowest with the most effective sensitiser, as shown in Fig. 2.

The kinetics appears to be decided by the slower of at least two consecutive reactions, *e.g.* (i) that of the removal of the stabilising group from the leuco-base by formaldehyde and (ii) that of oxidation of the true leuco-base deprived of the stabilising group, by means of oxygen. This aspect of the work is now being studied.

ACKNOWLEDGEMENT

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SUMMARY

The sensitivity of the reaction between formaldehyde and leuco-methylene blue has been found to be increased in the presence of ethyl alcohol, acetone, diethyl ketone and methyl ethyl ketone. Acetone has been found to be most effective.

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Sensitisers increase the absorption maximum and stabilise it, while the rate of development of methylene blue colour is slowed down.

Sensitivity also depends upon the content of thiosulphate used to prepare the leuco-base; a smaller amount of thiosulphate increases greater sensitivity.

RÉSUMÉ

La sensibilité de la réaction entre la formaldéhyde et le dérivé leuco du bleu de méthylène augmente en présence d'alcool éthylique, d'acétone, de diéthylcétone et de méthyléthylcétone. L'acétone semble la plus active. Ces sensibilisateurs augmentent l'absorption maximum et stabilise la réaction, tandis que la vitesse de formation du bleu de méthylène diminue. La sensibilité dépend également de la quantité de thiosulfate, utilisée pour préparer la leuco-base.

ZUSAMMENFASSUNG

Es wurde gefunden, dass die Empfindlichkeit der Reaktion zwischen Formaldehyd und Leukomethylenblau in Gegenwart von Äthylalkohol, Aceton, Diäthylketon und Methyläthylketon zunimmt. Am wirkungsvollsten erwies sich Aceton. Sensibilisatoren erhöhen das Absorptionsmaximum und stabilisieren es und setzen die Geschwindigkeit der Entwicklung der Methylenblaufärbung herab. Die Empfindlichkeit hängt ebenfalls von der Menge des bei der Herstellung der Leukobase benützten Thiosulfats ab. Eine geringere Menge Thiosulfat erhöht die Empfindlichkeit.

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THE USE OF THE MOLYBDENUM ELECTRODE AS INDICATOR FOR HYDROGEN IONS

by

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The molybdenum electrode was applied by some authors as indicator for hydrogen ions in acid-base titrations. LIFSCHITZ AND REGGIANI[1] preferred molybdenum to tungsten electrodes for measurements in acid but not in alkaline solutions in which they inferred that molybdenum showed passivity. BRINTZINGER AND ROST[2] used molybdenum and tungsten electrodes in potentiometric titrations in place of hydrogen, quinhydrone, glass, and antimony electrodes after subjecting them to a variety of treatments. Before use the electrodes were tested and empirical curves prepared with buffer solutions of known pH. They inferred that molybdenum was better than antimony and the divergence from the theoretical values was not, as a rule, more than 0.1 pH unit. ABICHANDANI AND JALKER[3] showed that molybdenum electrodes gave a theoretical relation only between pH 5 and 7. The work of these latter authors appears to contradict the usefulness of the molybdenum electrode in pH measurements as it restricts this to the pH range 5 to 7. We therefore tried to find out from a study of the electrodic behaviour of molybdenum in buffer solutions, the limit of pH within which the electrode can function as an indicator for H^+ -ions, by constructing time-potential and pH-potential relations. The accuracy of molybdenum to function as such can further be checked by determining the titration end-points and pK_a values of some acids from neutralisation curves performed with the aid of that electrode.

EXPERIMENTAL

The electrodes

The molybdenum electrodes consisted of wires, 2 mm in diameter and $1\frac{1}{2}$ cm in length, welded to glass tubings that could be filled with mercury for making the electrical contact. The metal was a spectroscopically pure sample supplied by Johnston and Matthey, England. Six electrodes were used, four of which were always polished before each titration, whereas the other two were left for a long time without polishing, so that they were covered with a black layer of the oxide.

The buffer solutions

The buffer solutions used for the potential measurements were the Clark and Lubs buffers (pH 1 — 10)[4], the McIlvain buffers (pH 2 — 3)[5] and the Ringer buffers (pH 11 — 12)[6]. These we rechecked by the hydrogen electrode, and in the case of the acid buffers with the quinhydrone electrode as well. The acids titrated included hydrochloric, sulphuric, nitric, acetic, boric, oxalic, malonic, succinic, tartaric, maleic, citric and phosphoric acids. These were of the analytical reagent grade except boric acid which was purified by several recrystallisations of a pure product and then dried over $CaCl_2$ in a desiccator till constant weight. The solutions were prepared by dissolving the appropriate amount in twice distilled water. The normalities of the strong acids were determined using sodium carbonate. All acids were also standardised with well prepared and checked sodium hydroxide solutions, using phenolphthalein as indicator.

The sodium hydroxide solutions

These were prepared by diluting a more concentrated one ($\sim 18N$) free from carbonate, with CO_2-free water in an atmosphere of N_2. They were standardised with potassium hydrogen phthalate, using phenolphthalein as indicator.

All potential measurements were made at a constant temperature in air or water thermostats adjusted at 35° C ± 0.05°.

The titration device and working procedure

The titration vessel was essentially similar to that previously described[7].

In performing an experiment 25 ml of the acid were placed in the titration vessel. The sodium hydroxide solution was added from a special device, and the change in the hydrogen ion concentration followed potentiometrically with the aid of molybdenum electrodes. Before beginning the titration the electrodes were left immersed in the solution for 90 minutes to attain thermal equilibrium. This time was found to be sufficient for the attainment of steady state potentials (see Fig. 1). Equilibria were rapidly attained after each alkali addition but a period of 5 min was always allowed for the mixing of the solutions to occur. Stirring was performed by bubbling either air free from CO_2 or

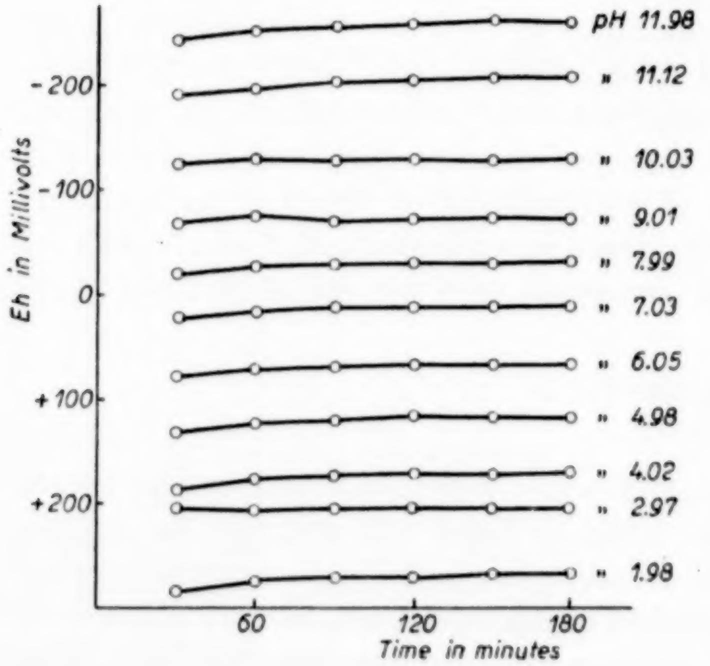

Fig. 1.

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nitrogen purified according to the method of HARCOUT AND LUPTON[8].

In constructing the calibration curves two methods were applied. In one of these, the potentials set up by molybdenum electrodes in the buffer solutions, 90 min after immersion, were plotted against pH. In the other method the pH-potential relation was constructed from neutralisation curves of the universal buffer mixture of BRITTON AND ROBINSON[9] using the molybdenum electrode. The pH of the solution at each alkali addition was measured by the hydrogen electrode in a separate titration. Although the neutralisations were performed with polished and aged electrodes both in presence of air or nitrogen, the determination of pK_a was restricted to polished electrodes in aerated solutions. Under these latter conditions the results were quite reproducible and the pK_a values comparable with those of other authors. In the presence of nitrogen the pK_a values were not good. This is due to the fact that the potentials set up by the molybdenum electrode as found by one of us (to be published elsewhere) depend much on the partial pressure of oxygen in solution. This makes it difficult to obtain, in the presence of nitrogen, comparable results between the neutralisation of acids and that of the universal buffer mixture used for calibration.

RESULTS

The effect of time on the electrode potential

As may be seen from the results shown in Fig. 1, it is apparent that the potentials set up by the polished molybdenum electrodes in aerated buffer solutions manifest steady state values from the time of immersion, with but slight changes, amounting at a maximum to 15 mv over a period of 180 min. This indicates that the molybdenum electrode is quite suitable for carrying out neutralization processes as no drifts in potential are liable to take place when the pH of the solution changes during titration.

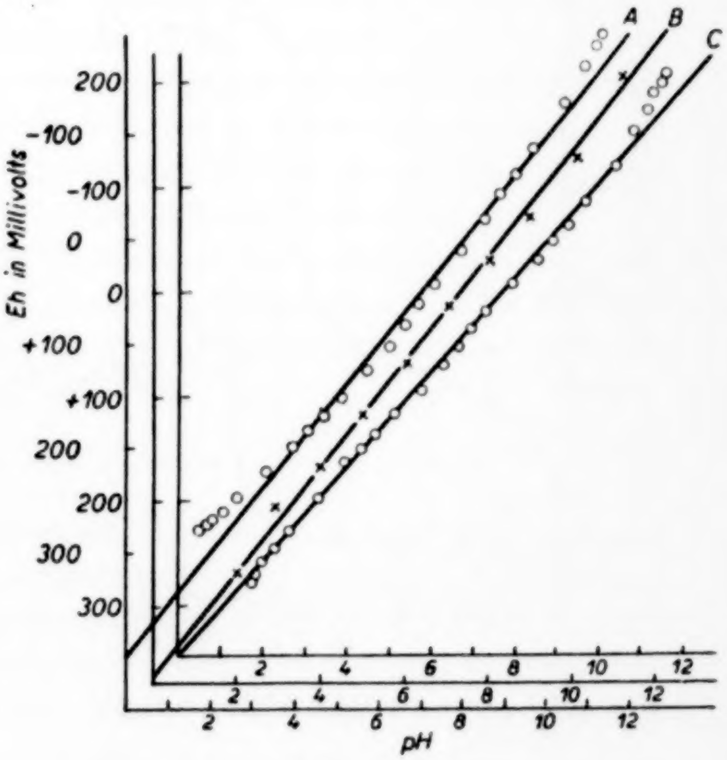

Fig. 2.

The pH potential relation

By plotting the potentials given by the above electrodes 90 min after immersion in the buffer solutions, curve B shown in Fig. 2 is obtained. From this curve it is clear that within the pH range 2 — 11 there is a linear relation between pH and potential, indicating that the electrode could be safely used, within this pH range as an indicator for H^+-ions. The slope of this curve amounts to 51 mv/pH unit, deviating thus from that of the hydrogen electrode. Curve C (Fig. 2) obtained by neutralizing the universal buffer mixture under aerated conditions, although representing a linear potential-pH relation, possesses a slope smaller than in the previous case and amounting to only 45.5. Curve A (Fig. 2) obtained also by neutralizing the same universal buffer mixture but in an atmosphere of nitrogen is not quite regular. The slope of the best straight line passing through the points amounts to 50. Although, as such, molybdenum electrodes cannot be used in oxygen-free solution for accurate pH measurements, with their aid, the neutralization of acids can be performed potentiometrically with a reasonable jump at the end-point.

The neutralization curves

From the neutralization curves of the above acids some of which are shown in Figs. 3 to 5 the following conclusions could be drawn:

Steep inflections in the region of the end-point amounting on an average to about 400 millivolts are obtained in case of hydrochloric, nitric and sulphuric acids. The end-points coincided quite closely with the equivalence points irrespective of other conditions such as the nature of the electrode or prevailing atmosphere. Acetic acid yielded an excellent curve with an inflection at the end-point amount-

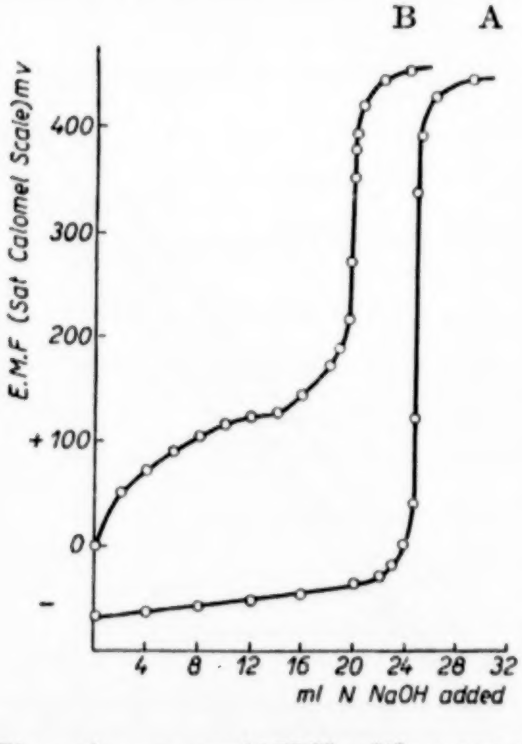

Fig. 3 A = 0.100N HCl with 0.2015N NaOH
B = 0.0996N CH_3COOH with 0.2015N NaOH

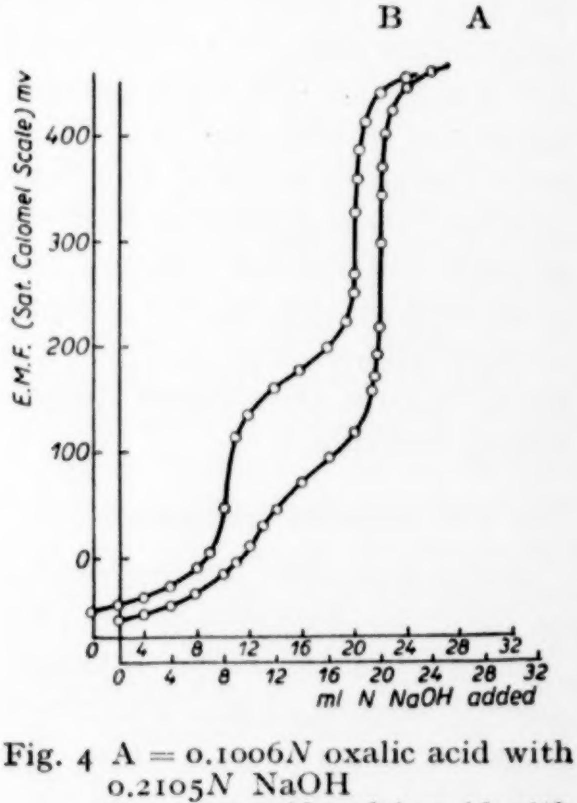

Fig. 4 A = 0.1006N oxalic acid with 0.2105N NaOH
B = 0.2034N maleic acid with 0.2105N NaOH

ing to 200 millivolts. The end-points coincided in air whereas in nitrogen atmosphere they occurred 0.75% earlier. The titration curve of boric acid shows but a very weak inflection. Succinic and tartaric acids, although dibasic, manifest but one inflection point corresponding to the second step of ionization. Oxalic and malonic acids show two inflections, the first of which is not sharp enough to permit a determination of the inflection point, while the second is quite sharp covering a range of 200 millivolts. Maleic acid in contradistinction to the other dibasic acids investigated yielded a titration curve with two sharp inflections amounting to 100 and 200 millivolts, respectively. Citric acid showed but a single inflection corresponding to the third stage of ionization. Phosphoric acid yieldep two sharp inflections corresponding to the first and second steps of ionization. The first of these inflections coincided fairly satisfactory with the theoretical equivalence point in oxygen-free solutions. In aerated solutions it occurred 1% late. The second step occurred somewhat late under all conditions.

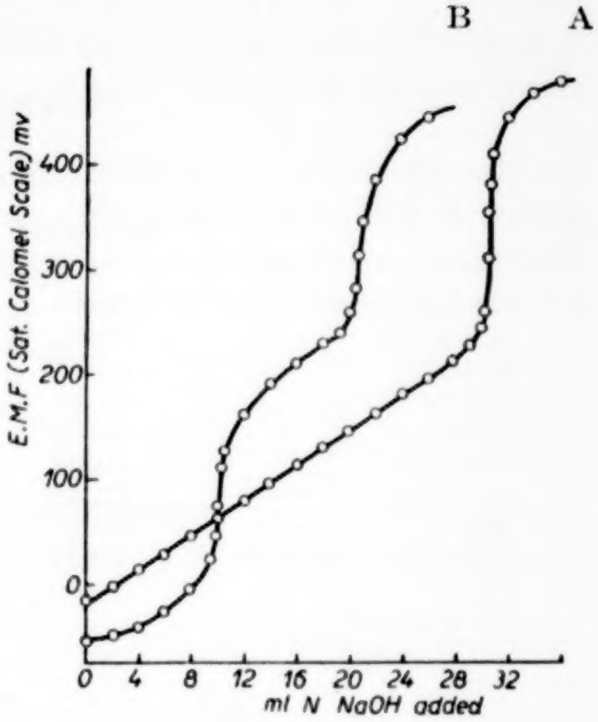

Fig. 5 A = 0.3081N citric acid with 0.2015N NaOH
B = 0.02024N phosphoric acid with 0.2015N NaOH

For the sake of comparison, the theoretical volumes of alkali and the ones consumed in titration of the different acids, together with the % error, are shown in Tables 1A and 1B, from which it is quite apparent that the electrode is quite sensitive in determining the end-points in neutralization reactions.

As a further check for testing the applicability of the molybdenum electrode as a pH indicator, we determined the pK_a values corresponding to the different neutralization stages of the weaker acids titrated. For this purpose we used the approximate HENDERSON-HASSELBALCH[10] relation:

$$\mathrm{pH} = \mathrm{p}K_a' + \log\,[\text{salt}]/[\text{acid}] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

in which the terms [salt] and [acid] correspond to the % of the neutralized and the unneutralized portions of the acids, respectively, pK_a' represents the classical dissociation constant and not the thermodynamic one, since the values of [salt] and [acid] are considered in terms of concentrations and not of activities. The values of pH to be substituted in equation (1) can be calculated from the following relation:

$$E_{\mathrm{H}} = E_o' - x\ \mathrm{pH} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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TABLE I A

POLISHED ELECTRODES

Acid	End-point by indicator	Observed end-point in air	Error %	Observed end-point in nitrogen	Error %
Hydrochloric	24.80	24.75	0.20	24.73	0.23
Nitric	25.00	25.01	0.04	24.96	0.16
Acetic	19.85	19.80	0.22	19.70	0.75
Sulphuric	25.10	25.08	0.08	25.18	0.31
Oxalic	20.00	19.97	0.15	19.93	0.35
Malonic	19.95	20.00	0.25	19.98	0.15
Succinic	19.95	19.90	0.26	19.98	0.15
Maleic	20.20	20.18	0.10	20.15	0.25
Tartaric	19.85	19.92	0.25	19.88	0.15
Citric	30.60	30.68	0.25	30.65	0.16
Phosphoric					
1st step	10.05	10.15	1.00	10.02	0.30
2nd ,,	20.10	20.60	2.43	20.30	1.00

TABLE I B

AGED ELECTRODES

Hydrochloric	24.80	24.62	0.09	24.83	0.12
Nitric	25.00	25.01	0.04	25.01	0.04
Acetic	19.85	19.79	0.30	19.70	0.75
Sulphuric	25.10	25.09	0.04	25.18	0.31
Oxalic	20.00	20.04	0.20	19.95	0.25
Malonic	19.95	20.00	0.25	20.02	0.35
Succinic	19.95	19.89	0.30	20.02	0.35
Maleic	20.20	20.22	0.10	20.18	0.10
Tartaric	19.85	19.92	0.35	19.90	0.25
Citric	30.60	30.70	0.33	30.67	0.23
Phosphoric					
1st step	10.05	10.25	2.00	10.15	1.00
2nd ,,	20.10	20.60	2.43	20.25	0.74

in which E_H represents the potentials (relative to the hydrogen electrode) set when 40, 50 and 60% of the acid are neutralized. E_o', which represents the potential of the molybdenum electrode at unit H^+-ion activity, can be evaluated by extrapolating the pH-potential relations (curves B, C, Fig. 2) to pH = 0. By so doing E_o' values amounting to 370 and 350 mv were obtained in the case of aerated buffer solutions and the universal buffer mixture respectively. x which represents the potential-pH gradients, $\triangle E/\triangle$pH, of the two curves amounts to 51 and 45.5, respectively. Substituting for the above terms in relation (2), we calculated the pH values of the solution at three stages of neutralization, *viz.* when 40, 50 and 60% of the acid have been neutralized. By applying equation (1) and substituting for pH, and for the ratio of the [salt]/[acid], pK_a' values were obtained as listed in Table II. These represent the mean of values obtained at the three neutralization stages which did not deviate from each other by more than 0.1 pH unit.

Comparison of these values with those obtained by other authors reveals fair agreement in most cases. With exception of citric and boric acids the deviation between our values and those reported by other authors amounts to a maximum of 0.2 pK_a unit. These deviations may be attributed to the possible interaction between the electrode material and these acids.

TABLE II

Acid	Mean pK_a[1]	Mean pK_a[2]	pK_a reported by other authors	
Acetic	4.936	4.797	4.754[9] ,	4.754[10]
Boric	9.645	9.007	9.26[11] ,	9.20[12]
Oxalic				
1st step	1.945	1.836	2.00[13] ,	1.42[14]
2nd ,,	4.302	4.235	4.39[14] ,	3.9[15]
Malonic				
1st step	2.732	2.831	2.844[16] ,	2.70[14]
2nd ,,	6.028	5.774	5.657[16] ,	
Succinic				
1st step	3.985	3.948	4.00[13] ,	
2nd ,,	5.689	5.474	5.595[16] ,	5.30[13]
Maleic				
1st step	1.759	1.961	1.93[14] ,	1.921[17]
2nd ,,	6.345	6.038	6.22[17] ,	5.9-6.6[18]
Tartaric				
1st step	2.692	2.817	2.90[13] ,	2.98[19]
2nd ,,	4.135	4.080	4.00[13] ,	4.39[14]
Citric	6.594	6.274	5.80[13]	
Phosphoric				
1st step	1.765	1.975	1.99[20] ,	
2nd ,,	6.959	6.634	6.81[20] ,	6.9[13]

[1] Molybdenum electrodes calibrated with buffer solutions.
[2] ,, ,, ,, ,, universal buffer mixture.

SUMMARY

The molybdenum electrode is found to act as a suitable means for the determination of the hydrogen ion concentration. Polished electrodes in aerated solutions give potentials which do not vary appreciably with time. The potential measured in solutions of different H+-ion activity is a function of pH from 2-11. pK_a values determined from neutralization curves of some acids are not much different from those obtained by other authors, using different methods. Polished or aged electrodes in aerated or oxygen-free solutions could be used satisfactorily for determining the end-points in neutralization reactions.

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RÉSUMÉ

Une électrode de molybdène peut être utilisée pour la détermination de la concentration en ions hydrogène. Les électrodes polies en solution aérée indiquent un potentiel constant. Les potentiels mesurés dans des solutions d'activités de H^+ différentes sont fonction du pH de 2 à 11. Les valeurs de pK_a de quelques acides, déterminées au moyen des courbes de neutralisation diffèrent peu des valeurs obtenues par d'autres auteurs utilisant d'autres méthodes. Ces électrodes polies ou usées, en solution, avec ou sans oxygène, peuvent être employées avantageusement pour déterminer les points finaux de réactions de neutralisation.

ZUSAMMENFASSUNG

Es hat sich herausgestellt, dass die Wasserstoffionenkonzentration sehr gut mit einer Molybdän-Elektrode bestimmt werden kann.

Polierte Elektroden in durchlüfteten Lösungen ergeben Potentiale, die sich mit der Zeit nicht wesentlich ändern. Das Potential, das in Lösungen von verschiedener Wasserstoffionenkonzentration gefunden wird ist eine Funktion des pH von 2-11. Unsere pK_a Werte von Neutralisationskurven verschiedener Säuren underschieden sich nicht wesentlich von den Werten anderer Autoren, die andere Methoden verwendeten. Es ist möglich, den Endpunkt von Neutralisationsreaktionen mit polierten oder gealterten Elektroden in durchlüfteten oder O_2-freien Lösungen zu bestimmen.

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SUR L'INTENSITÉ DU COURANT PENDANT UN TITRAGE „DEAD STOP". II

par

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Dans une publication antérieure[1], l'auteur était parvenu à déduire comment l'intensité du courant dépend, pour un titrage „dead stop", de la tension appliquée et de la quantité de réactif, tandis que nous allons rechercher maintenant dans quelle mesure la pratique satisfait aux exigences.

Avaient été contrôlés:

1. le rapport entre le courant et la tension pour une solution de concentrations de ferrocyanure et de ferricyanure égales;
2. le rapport entre l'intensité du courant et la dilution des solutions pour des concentrations de ferrocyanure et de ferricyanure identiques;
3. le rapport entre l'intensité du courant et la quantité de réactif ajouté pour les titrations suivantes:

a) arsénite, titré avec du ferricyanure dans l'hydroxyde de sodium 5.5N. Ce titrage avait déjà été effectué[2] dans un milieu moins fortement alcalin, mais à une température plus élevée, et à l'aide d'un indicateur rédox;

b) ferricyanure, titré dans le même milieu avec de l'arsénite ou de l'hydrazine[3]. Par l'accroissement de la concentration d'hydroxyde de sodium, la vitesse de réaction augmente à tel point qu'il est possible d'effectuer le titrage. Les résultats obtenus avec l'hydrazine sont si parfaitement identiques à ceux de l'arsénite, que nous ne donnerons ici que le mode opératoire;

c) ferricyanure, (additionné au préalable d'une quantité relativement grande de ferrocyanure) également titré avec de l'arsénite.

Le rapport doit donc être approximativement rectiligne, puisque l'hyperbole est suivie entre une valeur de x très voisine de 1 et la valeur 1.

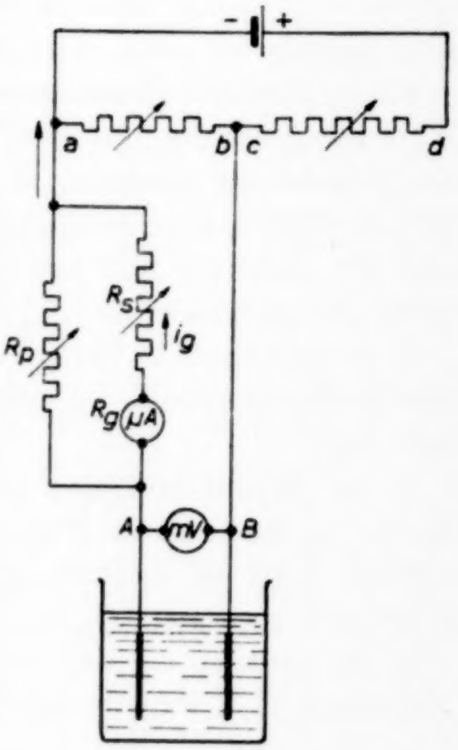

Fig. 1. Circuit électrique.

Le schéma utilisé (Fig. 1) ne diffère pas de celui qu'on emploie ordinairement[4], mais un millivoltmètre électronique (Philips GM 6010) est en outre branché sur les électrodes (2 petites plaques vibrantes en platine présentant une surface de 1 cm^2 environ et un écartement de 1 cm). La tension mesurée entre A et B est constamment corrigée (chute de tension dans la solution). Cette correction atteint parfois jusqu'à 10% de la tension mesurée, malgré la concentration anormalement élevée de l'électrolyte de base.

Tant que △ reste petit ($<$ 50 mV), le courant est proportionnel à la valeur corrigée; il en résulte que, dans les expériences suivantes, les corrections nécessaires pour rapporter l'intensité du courant à une valeur constante de △ sont simples.

De la 2ème expérience, il appert que le courant est proportionnel à la concentration dans un grand domaine de concentration. L'influence de la dilution qui se manifeste pendant un titrage peut donc être également facilement déterminée.

Dans notre cas, il est recommandé, pour ne pas rendre trop grande la correction de la tension, de maintenir à peu près constante la tension entre les électrodes à l'aide des deux potentiomètres ab et cd. Pour des titrages normaux, on maintient approximativement constante la tension entre a et b, en choisissant des petites valeurs pour les résistances ab et cd; en procédant de la sorte, le courant fourni par l'accumulateur est grand, comparativement à celui qui traverse l'électrolyte.

Pour calculer la valeur réelle de △, il faudrait de cette façon tenir compte aussi de la grande chute de tension dans le galvanomètre, y compris ses accessoires, et comme △ peut être plusieurs fois plus petit que la tension entre a et b, on obtiendrait pour △ une valeur fort peu précise, bien que ce mode de procéder ordinaire présente, pour les titrages normaux, l'avantage d'une simplicité beaucoup plus grande et celui d'un virage beaucoup plus subit.

Pour calculer l'abaissement de la tension dans la solution entre les électrodes, il est indispensable que la résistance R_x soit connue, puisque, en effet, l'intensité du courant est mesurée. R_x se révèle être égale à 1 Ω environ, de sorte qu'une mesure directe avec un appareil ordinaire de mesure de conductibilité ne donnerait que des résultats fort peu précis. Toutefois la résistance peut être déterminée, avec une précision de 1% environ, comme suit:

1. le récipient de titrage est rempli d'une solution de KCl 0.02*M* dont la conductibilité spécifique $\varkappa_{\mathrm{KCl}}$ est connue[5] et dont la résistance mesurée est exprimée par R_{KCl};

2. un second récipient pour la mesure de la conductibilité, d'une longueur de 40 cm environ et d'un diamètre intérieur de 0.3 cm, est rempli de H_2SO_4 2.176*N* dont on connaît également la conductibilité spécifique $\varkappa_{\mathrm{H_2SO_4}}$[4] et la résistance mesurée: $R_{\mathrm{H_2SO_4}}$;

3. la solution de KCl est transvasée dans ce petit récipient. On mesure la résistance R_x'. Puis on calcule alors la résistance cherchée R_x d'après la formule

$$R_x = R_x'.\ \frac{R_{\mathrm{KCl}} \cdot \varkappa_{\mathrm{KCl}}}{R_{\mathrm{H_2SO_4}} \cdot \varkappa_{\mathrm{H_2SO_4}}}$$

Ces mesures de résistance ont été effectuées à 1000 Hz avec l'appareil Philips GM 4249.

RÉSULTATS DES MESURES

1. 1 mmol $K_3[Fe(CN)_6]$ et 1 mmol $K_4[Fe(CN)_6].3H_2O$ dissous dans 100 ml NaOH 5.5*N*, température 25° C. Galvanomètre Pye „Scalamp" No. 7901/S. $R_g = 22.8$ Ohms.

Sensibilité du galvanomètre pour divers domaines de mesure:

$S = 1/1$: $5.85 \cdot 10^{-8}$ A/degré

$S = 1/20$: $20 \cdot 6.19 \cdot 10^{-8}$ A/degré

$S = 1/100$: $100 \cdot 5.83 \cdot 10^{-8}$ A/degré.

Résistance entre les électrodes: 0.44 Ω

$$i = i_g \cdot \frac{R_p + R_g + R_s}{R_p} = i_g \cdot f$$

TABLEAU I (Figs. 2 et 3)

mV	*S*	*i* degrés	R_s Ω	R_p Ω	*f*	*i* μA	*i.R* mV	△ corrigé	$\sqrt{\triangle'}$	$\frac{\sqrt{\triangle'}-1}{\sqrt{\triangle'}+1}$
0.114	1	88.0	2.2	100	1.25	6.44	0.003	0.111	1.0022	0.00110
0.205	,,	132.2	22.2	,,	1.45	11.4	0.005	0.200	1.0039	0.00195
0.320	,,	121.0	122.2	,,	2.45	17.3	0.008	0.312	1.0061	0.00305
0.519	,,	105.7	322.2	,,	4.45	27.5	0.012	0.012	1.0099	0.0042
0.970	,,	104.0	722.2	,,	8.45	51.4	0.023	0.947	1.0186	0.0092
1.99	,,	97.5	1722.2	,,	18.45	105.2	0.05	1.94	1.0385	0.0189
2.97	,,	70.0	3722.2	,,	38.45	157	0.07	2.90	1.0581	0.0283
5.00	1	76.0	5722.2	,,	58.45	260	0.11	4.89	1.100	0.0476
5.00	1/20	139.5	32.2	100	1.55	268	0.12	4.88	1.100	0.0476
9.80	,,	135.5	32.2	25	3.20	537	0.24	9.56	1.205	0.0930
15.0	,,	57.5	232.2	,,	11.20	797	0.35	14.6	1.329	0.141
29.5	1/20	111.0	232.2	,,	11.20	1540	0.68	28.8	1.753	0.274
50.6	1/100	59.1	132.2	,,	7.20	2480	1.1	49.5	2.623	0.448
74.9	,,	81.0	132.2	,,	7.20	3400	1.5	73.4	4.18	0.614
98.9	,,	98.0	132.2	,,	7.20	4110	1.8	97.1	6.63	0.739
122	,,	69.5	232.2	,,	11.20	4540	2.0	120.5	10.45	0.828
144	,,	73.6	232.2	,,	11.20	4810	2.1	142	15.9	0.881
174	,,	76.8	232.2	,,	11.20	4960	2.2	172	28.5	0.932
193	,,	77.5	232.2	,,	11.20	5060	2.2	191	41.3	0.953
222	,,	78.0	232.2	,,	11.20	5090	2.2	220	72.7	0.974
258	,,	78.5	232.2	,,	11.20	5130	2.3	258	152.2	0.988
175	,,	76.5	232.2	,,	11.20	4995	2.2	173	29.07	0.934
98.0	,,	97.0	132.2	,,	7.20	4070	1.8	96	6.49	0.733
52.0	,,	60.5	132.2	,,	7.20	2540	1.1	50.9	2.69	0.459
14.9	,,	70.0	2.2	25	2.00	816	0.36	14.55	1.326	0.140
4.99	1/100	37.8	2.2	125	1.20	264	0.12	4.87	1.099	0.0475

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Dans le Tableau I sont relevées les observations, ainsi que les corrections et les valeurs de la fonction

$$\frac{\sqrt{\triangle'}-1}{\sqrt{\triangle'}+1}$$

Il appert que le rapport rectiligne entre

$$i \text{ et } \frac{\sqrt{\triangle'}-1}{\sqrt{\triangle'}+1}$$

dérivé théoriquement, s'applique dans la pratique dans un très vaste domaine.

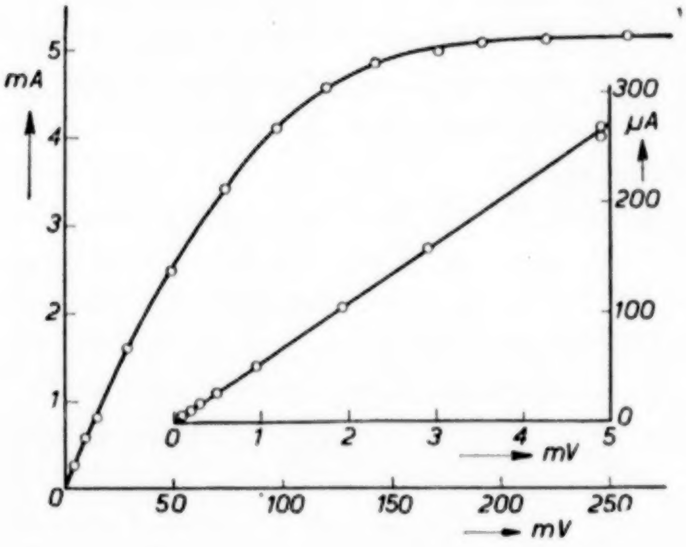

Fig. 2. Le courant en fonction de la tension corrigée.

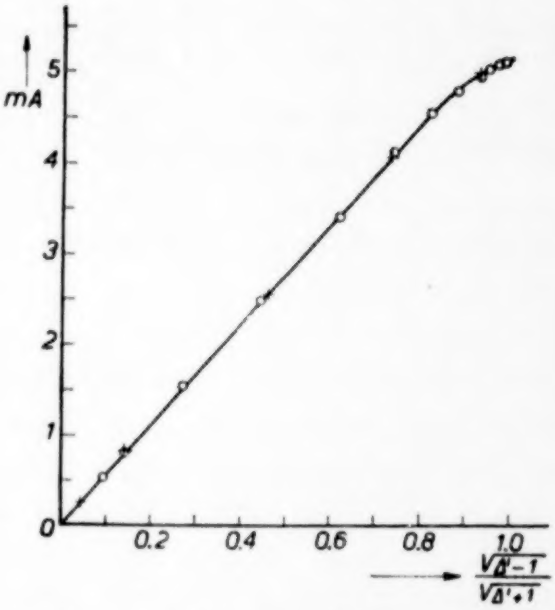

Fig. 3. Le courant en fonction de $\frac{\sqrt{\triangle'}-1}{\sqrt{\triangle'}+1}$

Nous pouvons également constater que, pour de petites tensions, le courant est proportionnel à $\triangle$; ceci facilite dans les expériences suivantes la réduction de l'intensité du courant à une valeur déterminée de $\triangle$.

2. La proportionnalité théorique à laquelle on peut s'attendre entre le courant maximum et la concentration est vérifiée entre autre en présence de bromure de potassium servant d'électrolyte de base (0.833*M*).

Les potentiomètres ab et cd ont été branchés de telle façon, qu'une différence de tension de 10.00 mV est constamment mesurée. Sensibilité du galvanomètre: 1/1. Résistance entre les électrodes: 1.35 Ω. Résistance R_p constante: 100 Ω.

Dans le Tableau II, les observations, de même que le rapport cherché, ont été relevés.

Pour des concentrations élevées, ce rapport s'avère plus grand que pour les concentrations moins élevées; ceci résulte probablement d'une influence de la migration.

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TABLEAU II

•C.10³ mol/l	*i* degrés	R_s Ω	*f*	*i* μA	*i.R* mV	△ corrigé	*i* corrigé	*i*/•C mA/mol/l
40	119.5	19877.2	200	1398	1.90	8.10	1726	43.2
20	67.0	,,	,,	784	1.06	8.94	877	43.8
10	36.0	,,	,,	821	0.57	9.43	447	44.7
5	122.5	2877.2	30	215	0.29	9.71	221	44.3
2.5	60.8	,,	,,	106.7	0.14	9.86	108	43.3
1.25	30.0	,,	,	52.6	0.07	9.93	53.0	42.4
0.625	112.5	277.2	4	26.3	0.04	9.96	26.4	42.3
0.312	56.5	,,	,,	13.2	0.02	9.98	13.2	42.3
0.156	27.8	,,	,,	6.51	0.01	9.99	6.51	41.7
0.078	44.5	2.2	5/4	3.25	0.00	10.00	3.25	41.7
0.039	18.0	,,	,,	1.32	0.00	10.00	1.32	42.5
0.020	9.0	,,	,,	0.66	0.00	10.00	0.66	41.4

Les corrections, devant être apportées dans les expériences suivantes pour la variation du volume pendant un titrage, peuvent être considérées toutefois comme étant proportionnelles à l'accroissement relatif du volume.

3a. Détermination de l'arsénite à l'aide d'une solution de ferricyanure titrée.

Pour maintenir constante le plus possible la conductibilité pendant le titrage, le ferricyanure a été dissous dans 5.5*N* NaOH. On est parti de As_2O_3 1/4 mmol dans 100 ml NaOH 5.5*N*.

Ferricyanure: 1/5 molaire. Résistance R_p constante: 100 Ω et R_s 2.2 Ω. Tension appliquée: 5.00 mV.

Sensibilité du galvanomètre: 1/20.

Résistance de l'électrolyte 0.44 ohm.

Dans le Tableau III figurent les autres données nécessaires pour la figure 4, dans laquelle les observations relevées dans le Tableau III sont indiquées par un o, tandis que les points x indiquent une autre série d'observations de même nature.

TABLEAU III (Fig. 4)

ml	*y*	*i* degrés	R_s Ω	*f*	*i* μA	*i.R* mV	△ corrigé	*i* corrigé	j_1
5.00	0.004	2.9	2.2	5/4	4.49	0.00	5.00	4.71	0.016
5.25	0.054	20.6	,,	,,	31.9	0.01	4.99	33.7	0.112
5.50	0.104	37.0	,,	,,	57.2	0.03	4.97	60.7	0.203
6.00	0.205	64.2	,,	,,	99.0	0.04	4.96	105.8	0.353
7.00	0.406	133.0	277.2	4	166	0.07	4.93	177	0.592
8.00	0.606	41.5	,,	,,	205	0.09	4.91	226	0.754
10.00	1.008	53.5	,,	,,	265	0.12	4.88	298	1.005
12.50	1.510	62.4	,,	,,	309	0.14	4.86	358	1.193
15.00	2.012	67.6	,,	,,	335	0.15	4.85	397	1.324
17.50	2.514	70.9	,,	,,	351	0.15	4.85	425	1.419

Trouvé par extrapolation que le point d'équivalence est situé à 4.98 ml et par interpolation que $i_1 = 297$ μA.

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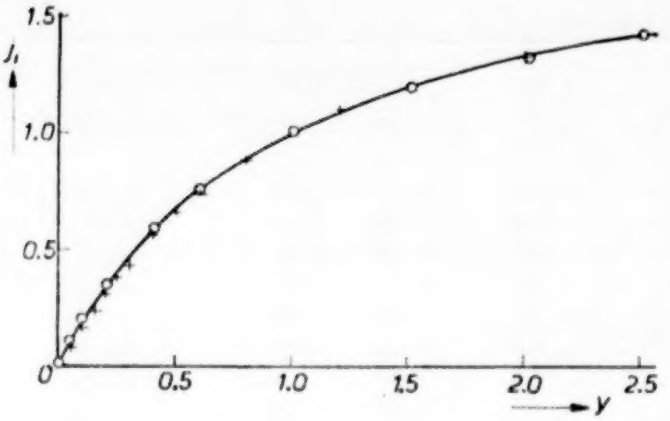

Fig. 4. Le courant relatif en fonction de l'excès de réactif.

La ligne indique le développement théorique.

Dans la colonne 9 figure la valeur de l'intensité du courant, corrigée par rapport à △ = 5.00 mV et pour un volume de 100 ml.

3b. Le titrage de 1 mmol de ferricyanure de potassium avec l'arsénite a été effectué également dans un électrolyte de base: hydroxyde de sodium 5.5*N*.

La solution d'arsénite est rendue fortement alcaline pour conserver le même milieu pendant toute la durée du titrage.

Volume initial: 100 ml. R_s = 22 ohms, R_p = 100 ohms, *S* = 1/20. Résistance entre les électrodes: 0.44 ohm; f = 5/4.

Nous donnons deux séries d'observations : dans la première, la tension entre les électrodes est maintenue à peu près constante à 5 mV; le titre de la solution d'arsénite est 0.4*N* (Tableau IV). Ici aussi, l'intensité du courant relevée dans la colonne 8 est corrigée par rapport à 5.00 mV et au volume de 100 ml.

TABLEAU IV (Fig. 5)

ml	*x* %	mV	*i* degrés	*i* μA	*i.R* mV	△ corrigé	*i* corrigé	*jm*
0	1.21	5.00	5.0	7.74	0.00	5,00	7.68	0.0529
0.10	5.23	5.07	19.5	30.2	0.01	5.06	29.8	0.206
0.20	9.25	5.04	32.1	49.7	0.02	5.02	49.6	0.342
0.30	13.28	5.08	43.7	67.6	0.03	5.05	67,1	0,461
0.50	21.32	5.06	63.4	98.1	0.04	5.02	98.2	0.677
0.75	31.38	5.15	81.9	126.7	0.06	5.09	125.4	0.865
1.00	41.44	5.14	91.9	142.2	0.06	5.08	141.4	0.975
1.25	51.50	5.10	93.2	144.2	0.06	5.04	144.8	0.999
1.50	61.55	5.16	90.0	139.3	0.06	5.10	138.6	0.957
1.75	71.63	5.11	76.7	118.5	0.05	5.06	119.2	0.822
2.00	81.67	5.09	57.6	89.3	0.04	5.05	90.2	0.622
2.25	91.74	5.05	30.8	47.7	0.02	5.03	48.5	0.334
2.30	93.76	5.08	23.2	35.9	0.02	5.02	36.6	0.252
2.35	95.76	5.03	16.7	25.8	0.01	5.02	26.3	0.182
2.40	97.77	5.04	8.0	12.4	0.00	5.04	12.6	0.087
2.45	99.80	5.04	0.9	1.39	0.00	5.04	1.41	0.010

Trouvé par extrapolation que le taux initial en ferrocyanure est équivalent à 0.030 ml d'arsénite et que le point équivalent est situé à 2.455 ml.
Le courant maximum i_m est 145.0 μA.

Dans la deuxième série, où le titre de l'arsénite est 0.2*N*, les résistances ab et cd ne varient pas, de sorte que la tension entre les électrodes varie fortement (Tableau V). Les résultats de ces deux tableaux sont reproduits dans la Fig. **5**. La

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courbe expérimentale correspond bien au développement théorique. Le ferricyanure renfermant toujours une faible quantité de ferrocyanure, nous avons dû, dans un graphique à part, déduire le point de départ du titrage pour le cas où nous aurions eu du ferricyanure pur. De même, nous avons déterminé graphiquement le point final, ainsi que le courant maximum.

TABLEAU V (Fig. 5)

ml	x %	i degrés	mV	j_m sans corrections
0	1.0	3.5	5.00	0.058
0.50	11.0	29.5	4.26	0.486
1.00	21.0	45.0	3.80	0.750
1.50	31.0	54.0	3.54	0.890
2.00	41.0	59.0	3.36	0.972
2.50	51.0	60.6	3.31	0.998
3.00	61.0	58.5	3.35	0.964
3.50	71.0	53.0	3.46	0.873
4.00	81.0	43.4	3.72	0.715
4.50	91.0	25.9	4.20	0.427
4.60	93.0	21.1	4.32	0.348
4.71	95.2	15.2	4.47	0.250
4.80	97.0	10.9	4.59	0.180
4.90	99.0	3.6	4.78	0.059
4.95	100.0	0.5	4.84	0.008

Trouvé par extrapolation que le taux initiale en ferrocyanure est équivalent à 0.05 ml d'arsénite.
Le courant maximum est 60.7 degrés.
Les valeurs des résistances ab et cd sont respectivement 0.1 ohm et 348 ohms.

3c. Lorsqu'on titre un ferricyanure avec de l'arsénite, en présence d'un grand excès de ferrocyanure, on a le cas 3b, x variant alors entre une valeur légèrement plus petite que 1 et x = 1. Cette faible portion de la courbe doit être considérée comme approximativement rectiligne. Cette titration présente quelque analogie avec celle de l'iode par le thiosulfate en présence d'iodure.

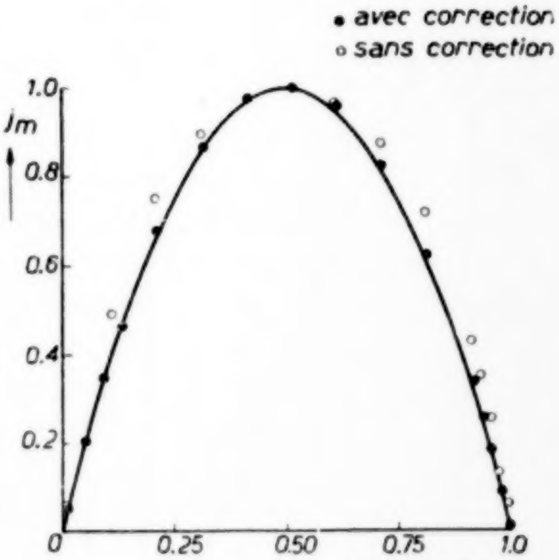

Fig. 5. Le courant relatif en fonction du réactif.

Composition de la solution: 1 mmol de ferricyanure de potassium, 25 mmol de ferrocyanure de potassium dans 100 ml d'hydroxyde de sodium 5.5N.

Résistance mesurée: 0.46 ohm.

Titre de la solution d'arsénite: 0.4N. R_s = 177.2 ohms.

R_p = 100 ohms ($j = 3$). $S = 1/20$.

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Dans le Tableau VI, les résultats sont donnés pour une tension sur les électrodes à peu près constante, tandis que l'intensité du courant est corrigée par rapport à $\triangle$ = 5.00 mV et pour un volume de 100 ml.

Dans le Tableau VII, les résistances ab et cd n'ont pas subi de changements pendant le titrage.

Ces deux tables sont reproduites dans la figure 6.

TABLEAU VI (Fig. 6)

ml	mV	*i* degrés	*i* μA	*i.R* mV	$\triangle$ corrigé	*i* corrigé μA
0	5.10	121.3	451	0.21	4.89	461
0.25	5.10	110.0	409	0.19	4.91	417
0.50	5.00	95.6	355	0.16	4.94	369
0.75	5.16	85.3	317	0.15	5.01	318
1.00	5.20	73.0	271	0.12	5.08	270
1.25	5.00	57.4	213	0.10	4.90	220
1.50	5.15	45.1	168	0.08	5.07	168
1.75	4.98	30.4	113	0.05	4.93	117
2.00	5.00	16.4	60.9	0.03	4.97	62.5
2.10	5.12	11.4	42.3	0.02	5.10	42.4
2.20	5.10	5.6	20.8	0.01	5.09	20.9
2.30	5.00	0.6	2.2	0.00	5.00	2.2

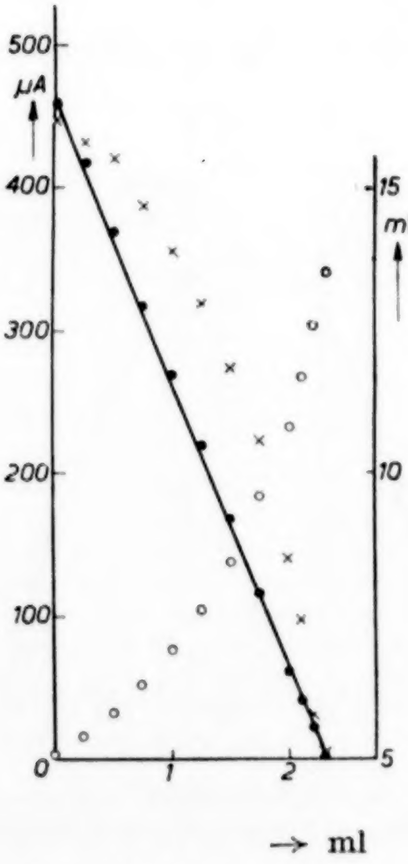

TABLEAU VII (Fig. 6)

ml	mV	*i* degrés	*i* μA
0	5.10	120.5	448
0.25	5.43	116.5	433
0.50	5.80	111.0	412
0.75	6.29	104.1	387
1.00	6.90	95.7	356
1.25	7.59	86.0	320
1.50	8.43	73.8	274
1.75	9.60	56.9	212
2.00	10.8	38.0	141
2.10	11.7	26.3	97.8
2.20	12.6	13.9	51.6
2.30	13.5	1.0	3.7

Fig. 6. Le courant corrigé et non corrigé × et la tension mesurée ○ en fonction du volume d'arsénite, en présence d'un grand excès de ferrocyanure.

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RÉSUMÉ

Les conclusions théoriques du titrage „dead stop" pour un système réversible, ont été démontrées par une série d'essais effectués au moyen du système ferri-ferrocyanure.

Ceci confirme les hypothèses de DELAHAY[7].

SUMMARY

The mathematically deduced formulae for dead-stop titration agree with the results obtained for the ferrocyanide-ferricyanide system.

This confirms DELAHAY's[7] hypotheses.

ZUSAMMENFASSUNG

Die mathematisch abgeleitete Formeln sind in Übereinstimmung mit der Beobachtung im Falle des Systems Ferri-Ferrozyanid.

Zugleich ist es eine Bestätigung der Auffassung DELAHAY's[7].

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THE POLAROGRAPHIC ESTIMATION OF MOLYBDENUM IN PLANT MATERIALS

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INTRODUCTION

The principal method of determining molybdenum in plant materials has been that of measuring the colour of the molybdothiocyanate complex, there being several modifications to the basic method. The minimum quantity of molybdenum measurable with any certainty is in the region of one microgram. A more recent development is the dithiol colorimetric procedure[1,9] which is capable of measuring 0.2 μg.

Until recently the literature has provided few polarographic methods for molybdenum which are in any way superior to the colorimetric methods. This is due to the fact that the sensitivity of the normal molybdenum wave is comparable with that of the colorimetric methods. Good selectivity was achieved by PRIBIL AND BLAZEK[10] who used a supporting electrolyte of ammonium acetate - acetic acid containing ethylenediaminetetra-acetic acid (EDTA) which caused the suppression of the waves of most of the interfering metals.

By the use of supporting electrolytes in which molybdenum gives rise to catalytic waves where the catalytic current is as much as 10 times greater than the normal diffusion current, and providing any possible interfering metals are absent, the sensitivity of the polarographic estimation of molybdenum can be greatly increased (see below). JOHNSON AND ROBINSON[6] measured the catalytic wave in 0.1M H_2SO_4, 0.2M Na_2SO_4, while HAIGHT[5] measured an even greater catalytic wave in 0.75M H_2SO_4, 1M $HClO_4$ while estimating molybdenum in steels.

Thus by utilising the principle of the catalytic wave in a modification of HAIGHT's[5] method in combination with a selective extraction process, a highly sensitive procedure for the estimation of molybdenum has been developed and found to be very successful in practice: α-benzoinoxime in dilute sulphuric acid is used as an extractant and the perchloric acid is replaced by sodium perchlorate in the supporting electrolyte.

POLAROGRAPHIC REQUIREMENTS

According to KNOWLES[7] the metals that react with α-benzoinoxime in dilute acid solution are Mo^{+6}, V^{+5}, Cr^{+6}, tungsten, palladium and tantalum. In addition copper reacts in alkaline solution. Consequently the polarographic behaviour of these metals (except Pd and Ta) was examined in the $0.75M$ H_2SO_4, $1M$ $HClO_4$ electrolyte.

In the presence of sulphuric acid molybdenum gives three waves but in the presence of perchlorate the reduction of Mo^{+4} to Mo^{+3} indicated by the third wave becomes catalysed owing to the reoxidation of Mo^{+3} to Mo^{+4} which is available for further reduction at the dropping mercury electrode. The polarographic wave becomes a catalytic wave and is not diffusion-controlled but is rate-controlled, and its magnitude depends to some extent on the concentration of perchlorate, reaching a tenfold increase over the diffusion current when molar perchlorate is used. In this electrolyte the third wave for molybdenum is measured at −0.21 v.V S.C.E.

Vanadium and chromium give no wave at all while iron gives a small wave from the first application of the voltage, but HAIGHT[5] overcomes this by reducing the iron to the ferrous state when estimating molybdenum in steels. Tungsten produces no wave in this electrolyte, although LAITINEN AND ZIEGLER[8] reported that tungsten gives a catalytic wave in $12M$ $HClO_4$ that is 100 times the diffusion current. They showed that in $HClO_4$ weaker than $9M$ this wave disappears. This was confirmed in the present work, and in the $0.75M$ H_2SO_4, $1M$ $HClO_4$ electrolyte no interference from tungsten was experienced. However, GEYER[4] noted that the presence of large quantities of tungstic acid are undesirable as with its low solubility it becomes precipitated and adsorbs some molybdenum. In the present investigation with 100 μg of tungsten the molybdenum wave was reduced by 4 per cent. but with 50 μg of tungsten there appeared to be no adsorption of molybdenum. The chances of there being more than 50 μg of tungsten present in the extract of a plant digest are fairly remote.

The only two common metals that do produce seriously interfering waves are copper (−0.05 v.V S.C.E.) and bismuth (−0.13 v.V S.C.E.), but under the conditions recommended neither metal is extracted by α-benzoinoxime. Even though the copper wave is only 1/8 the size of the molybdenum wave for equivalent quantities of metal, for very small amounts of molybdenum freedom from copper is important, so it is essential that there should be no copper present in the reagents used subsequent to the α-benzoinoxime extraction.

The supporting electrolyte recommended by HAIGHT[5] is $0.75M$ H_2SO_4, $1M$ $HClO_4$. In this work the $HClO_4$ is replaced by $NaClO_4$ since the latter is more readily prepared in the pure state and the characteristics of the molybdenum wave are the same. The electrolyte may be prepared by mixing 0.2 ml concentrated H_2SO_4 and 4.8 ml M $NaClO_4$ making a total volume of 5 ml. The 0.2 ml of H_2SO_4 is near enough to 7 drops from a conventional dropping bottle and may constitute the H_2SO_4 residue from the digestion of the organo-metallic extract. The ratio of sulphate to perchlorate should not be altered greatly, and the concentration of sulphate should not be increased above 1.1*M* otherwise the wave height will decrease.

For routine quantitative work it is more convenient to use a mercury pool anode than a saturated calomel electrode. Since the former anode has an anode potential of +0.2 v. in the $H_2SO_4.NaClO_4$ solution, the $E\frac{1}{2}$ value for molybdenum becomes −0.41 v., while in the $H_2SO_4.HClO_4$ solution with an anode potential of +0.35 v. the $E\frac{1}{2}$ value becomes −0.56 v. V anode pool.

Since the catalytic reduction of molybdenum at the dropping mercury electrode is not diffusion-controlled it is not surprising to find that the currents measured are not quite linear with the concentration of the metal, particularly at higher concentrations. Actually over a range of lower concentrations the current is linear, but it is advisable to prepare a graph to cover a fairly wide range of microgram quantities of molybdenum (0 to 50 μg).

By controlling the conditions within close limits good reproducibility may be achieved and the recoveries of added quantities of molybdenum to various types of plant samples have been excellent. Under favourable conditions the smallest concentration of molybdenum that can be measured is 0.02 μg per ml, but at this level the accuracy is no greater than ±20%. 0.1 μg per ml may be measured quite readily ±5%.

EXTRACTION TECHNIQUE

First recommended by FEIGL[3] in 1923, α-benzoinoxime has been used as a reagent reasonably specific for copper, since in ammoniacal tartrate copper is one of the few metals precipitated by this compound. It was later noted by KNOWLES[7] that in 5% mineral acid Mo^{+6}, Cr^{+6}, V^{+5}, W, Pd and Ta are precipitated, and he published methods for the gravimetric estimation of molybdenum and tungsten in steels, eliminating the interference from chromium and vanadium by first reducing them to the Cr^{+3} and V^{+4} states with sulphur dioxide. For the analysis of steels DUNLEAVY, WIBERLEY AND HARLEY[2] extracted copper from tartrate solution at pH 11.3 with α-benzoinoxime and chloroform, but this reagent does not appear to have been reported previously as an extractant for any of the metals with which it is capable of chelating in dilute acid solution.

There was a temptation to apply the findings of PRIBIL AND MALAT[11] who precipitated Mo, W, U and V with 8-hydroxyquinoline in the presence of EDTA in acetate-acetic acid buffer, when all other cations including copper were completely screened. This principle cannot be applied to the extraction by chloroform of the molybdenum-α-benzoinoxime complex, since even small concentrations of EDTA completely prevent the extraction of both molybdenum and copper. However, in this medium sodium diethyldithiocarbamate (DDC) will extract molybdenum but it will also extract copper, indicating that the DDC complexes with molybdenum and copper are more stable than the EDTA complexes, but the α-benzoinoxime complexes with these two metals are less stable.

Molybdenum is completely extractable with α-benzoinoxime and chloroform from solutions containing acetate from pH 1 to pH 7 and probably at more alkaline reactions as well. Extraction is inhibited by tartrate over this range. In unbuffered solution it is completely extractable from 1% and 2% H_2SO_4 but incompletely from greater acidities, and the effect of increasing the acidity is shown in Table I.

TABLE I

THE EXTRACTABILITY OF MOLYBDENUM BY α-BENZOINOXIME AS INFLUENCED BY THE STRENGTH OF SULPHURIC ACID

Percentage H_2SO_4	Percentage extractability of Mo
1	100
2	100
3	92
4	77
7	69
10	61

The extracted molybdenum complex is colourless which is a slight disadvantage as no indication is available as to whether excess of the reagent is present.

Copper is not very readily extracted by α-benzoinoxime and chloroform as evidenced by the fact that DUNLEAVY *et al.*[2] found that in the presence of tartrate it was necessary to raise the pH to 11.3 before complete extraction could be achieved. Yet copper was found to be extractable to some extent in the presence of acetate at reactions as acidic as pH 2, but from 1% H_2SO_4 solution no copper is extractable (see Table II). Likewise no iron, vanadium or bismuth are extracted from this medium while tungsten is extracted to the extent of only 50%.

TABLE II

EXTRACTABILITY OF COPPER BY α-BENZOINOXIME AS INFLUENCED BY THE REACTION

Reaction	Percentage extractability
pH 4 (acetate buffered)	23%
pH 3 ,, ,,	7.5%
pH 2 ,, ,,	6.2%
pH 1 ,, ,,	0.4%
1% H_2SO_4 unbuffered	zero
2% H_2SO_4 ,,	zero

Finally 1% H_2SO_4 solution was regarded as a suitable medium for the extraction of molybdenum as copper and iron are eliminated, and the conditions may be conveniently reached following a wet digestion of plant materials using nitric, perchloric and sulphuric acids.

In the gravimetric estimation of molybdenum and tungsten, KNOWLES[7] guarded against the reduction of molybdenum to a lower state of valency by the α-benzoinoxime by adding bromine water. In this investigation extractions were carried out with and without bromine water with equal effectiveness, so providing the reaction is carried out within a few minutes of adding the reagent, the necessity of adding bromine does not arise.

REAGENTS

α-Benzoinoxime. 2% w/v solution in distilled ethanol, if stored in a refrigerator will keep for several months.

Sulphuric, nitric and perchloric acids. These should be distilled from pyrex stills. The chances of molybdenum being present as an impurity are slight but small quantities of copper would cause interference.

Sodium perchlorate 1M. Dissolve 14 g of $NaClO_4.H_2O$ in 100 ml glass-distilled water. It is essential that this solution be free of copper and molybdenum. If these metals are present the solution should be extracted with 8-hydroxyquinoline, the last traces of which must be removed by washing several times with chloroform.

Distilled water. Glass-distilled from pyrex equipment.

Standard molybdenum solution. Dissolve 0.184 g of pure $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 100 ml glass-distilled water. The strength should be checked gravimetrically by precipitation as lead molybdate. This solution contains 1,000 μg Mo per ml and should be diluted 100 fold and 1,000 fold for calibration standards.

APPARATUS

A Sargent model XXI polarograph employing Heyrovsky cells with mercury pool anodes is used. Oxygen is removed from the solutions by bubbling purified nitrogen. The cells are placed in a thermostatic water bath held at $25 \pm 0.1°$ C. All glassware is cleaned with 10% nitric acid and rinsed thoroughly with glass-distilled water.

PROCEDURE

For plant materials containing more than 1 p.p.m. of molybdenum 1 g of oven-dried material is used. For materials with smaller concentrations 5 or 10 g of the sample are taken and wet digested by means of sulphuric, nitric and perchloric acids. The quantity of sulphuric acid employed at this stage should be noted. Silica should be removed by centrifugation, and the solution is transferred to a separating funnel where the volume is adjusted so that the concentration of sulphuric acid falls between 1% and 2% v/v.

2 ml of α-benzoinoxime solution is now added and after being mixed thoroughly the solution is extracted with three 5 ml portions of chloroform which are collected in a test tube from which the chloroform is evaporated. 0.2 ml (7 drops) of concentrated sulphuric acid is added to the test tube where the extracted organic matter is decomposed by heating strongly with two or three 10-drop portions of nitric acid followed finally by two drops of perchloric acid.

The metallic residue dissolved in the sulphuric acid is transferred with rinsings to a small beaker in which the water is evaporated off on a hotplate at low heat. When the sulphuric acid fumes begin to be evolved the beaker is cooled and 4.8 ml of $1M$ $NaClO_4$ is added and after mixing thoroughly the solution is transferred to the polarographic cell through which purified nitrogen is bubbled for 10 minutes. The solution is polarographed from —0.1 v. to —0.8 v. V the anode pool. The molybdenum wave is measured and the catalytic current is compared with that found during a calibration run with known standards of molybdenum.

For very small quantities of molybdenum, bearing in mind the necessity of keeping the sulphate: perchlorate ratio reasonably constant, it is advisable to fume practically all of the sulphuric acid off the extracted metal in the beaker and then dissolve the molybdenum with gentle warming in 1 ml of the $0.75M$ H_2SO_4, $1M$ $NaClO_4$ electrolyte and finally polarograph the solution in a micro-cell.

ACKNOWLEDGEMENT

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SUMMARY

A method has been developed whereby molybdenum is extracted from digests of plant materials by means of α-benzoinoxime and chloroform from a medium of 1% sulphuric acid solution. Following the decomposition of the extract, the molybdenum is estimated polarographically by measuring the catalytic wave in a sulphuric acid-perchlorate supporting electrolyte in which the sensitivity is increased tenfold over the normal wave. The method provides a selective, highly sensitive procedure, capable of determining very small quantities of molybdenum.

RÉSUMÉ

Une méthode est proposée pour l'extraction du molybdène dans les végétaux, au moyen d'α-benzoïnoxime et de chloroforme, en solution d'acide sulfurique à 1%. Après décomposition de l'extrait, le molybdène est dosé polarographiquement en mesurant la vague catalytique obtenue, avec, comme solution de base, le mélange acide sulfurique-perchlorate (la sensibilité est ainsi augmentée de 10 fois). C'est une méthode sélective et très sensible permettant de doser de très petites quantités de molybdène.

ZUSAMMENFASSUNG

Es wurde eine Methode entwickelt bei der Molybdän aus digerierten Pflanzenmaterial mit Hilfe von α-Benzoinoxim und Chloroform aus 1%iger Schwefelsäurelösung extrahiert wird. Nach der Zersetzung des Extraktes wird Molybdän pola-

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rographisch durch das Messen der katalytischen Stufe in einem Schwefelsäure-Perchlorat enthaltenden Elektrolyt gemessen, in dem die Empfindlichkeit gegenüber der normalen Stufe um das Zehnfache grösser ist. Die Methode bildet ein selektives, höchst empfindliches Verfahren mit dem sehr kleine Mengen Molybdän bestimmt werden können.

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A NOTE TO THE ARTICLE "POLAROGRAPHIC REDUCTION OF GERMANIUM" by A. K. DASGUPTA AND C. K. N. NAIR[1]

by

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DASGUPTA AND NAIR stated[1], having read only the abstract of our paper[2] from Chemical Abstracts, that we fail to observe the second wave on reduction curves of tetravalent germanium in solutions, containing ammonia and ammonium chloride.

As is seen from Figs. 1 and 2, published also in our Czech paper[2], we observed both the waves of tetravalent germanium. Moreover, from our data we were able to draw conclusions concerning the nature of the electrode process corresponding to either wave.

The first wave is due to a four-electron reduction current, controlled by diffusion. The second wave, which at certain pH values has the form of a maximum, is of a catalytic nature. This is concluded from the increase of the height of the second wave when increasing the capacity of the ammonia-ammonium chloride buffer and when decreasing the pH. The catalytic nature of the second wave follows also from its occurrence mainly at higher concentrations of germanium (Fig. 1) and from its increase at longer drop-times (Fig. 2). Also the relatively

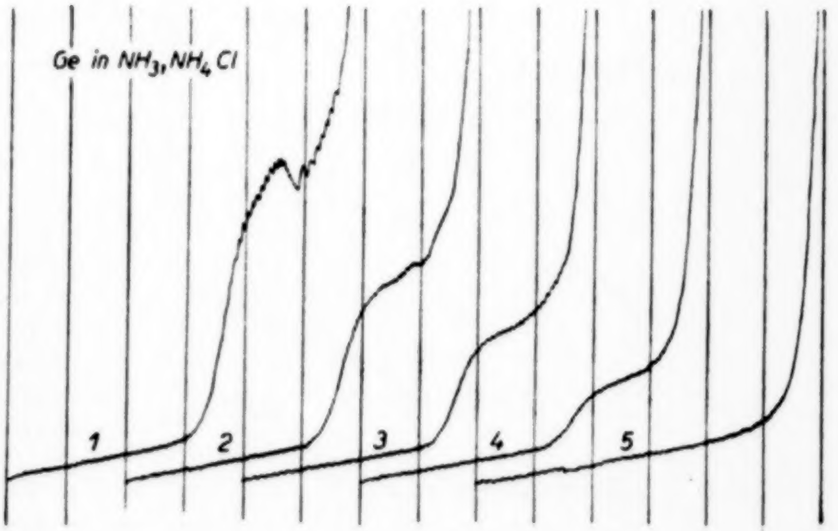

Fig. 1. The curves of tetravalent germanium in solutions containing ammonia and ammonium chloride. To 10 ml 0.1N NH$_3$ + 0.1N NH$_4$Cl a solution of Ge added. Solutions were prepared from a stock-solution, containing 0.2363 g germanium in 100 ml 0.1M KOH. Final concentrations: (1) 0 (2) $1.0 \cdot 10^{-5} M$ (3) $2.0 \cdot 10^{-5} M$ (4) $3.0 \cdot 10^{-5} M$ and (5) $5.0 \cdot 10^{-5}.M$ Curves registered from — 1.0 V.

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small effect of gelatin, observed by DASGUPTA AND NAIR[1], is in agreement with the above statement.

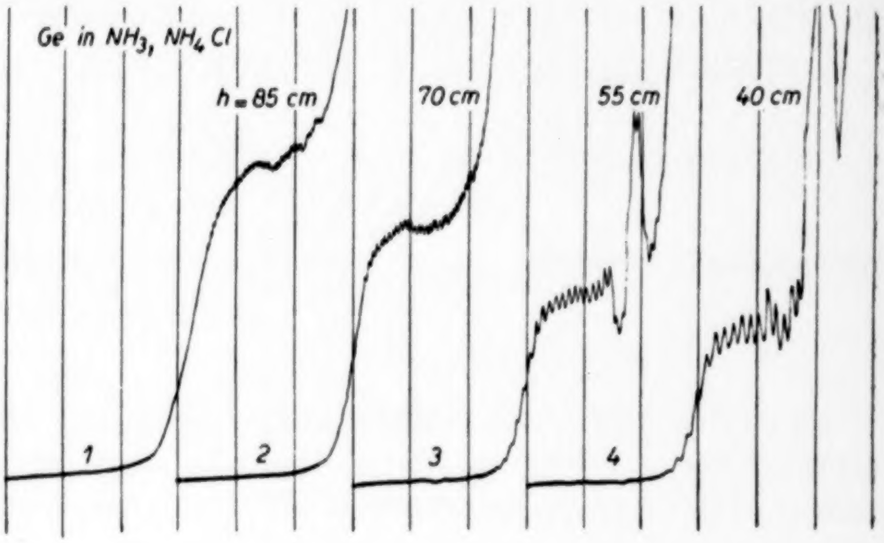

Fig. 2. The dependence of the waves of tetravalent germanium on the mercury pressure. $0.2N$ $NH_3 + 0.2N$ NH_4Cl containing $1 \cdot 10^{-4}M$ Ge. The height of mercury level: (1) h = 85 cm, (2) h = 70 cm (3) h = 55 cm (4) h = 40 cm. Curves are registered from —1.0V. Increase of maximum at longer droptimes.

The effect of gelatin on the height of the first wave (Fig. 4, ref.[1]) may be due to a suppression of a maximum of second kind[3-5] in presence of the relatively concentrated electrolyte.

The reduction curves at pH 6 and 7.5 (Fig. 1, ref.[1]) were obtained in poorly buffered solutions and the current may be also due to the reduction of protons, formed by hydrolysis.

We suppose that for analytical purposes it is preferable to measure not the total height of both waves as given by DASGUPTA AND NAIR[1], but only the height of the first wave[2]. It is better to use conditions[2] ($0.1N$ NH_3, $0.1N$ NH_4Cl $C_{Ge} < 3 \cdot 10^{-5}M$ and drop-time $t < 2.5$ sec at the rate of flow of mercury about m = 2 mg/sec) at which the second wave does not occur.

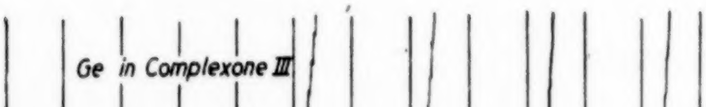

Fig. 3. Reduction of tetravalent germanium in a solution of Complexon III. $0.1M$ Complexon (ethylenediaminetetra-acetic acid) in a phosphate buffer solution of pH 7.8, with $1 \cdot 10^{-4}M$ fuchsin added. Germanium concentrations: (1) $2.8 \cdot 10^{-5}M$ (2) $5.6 \cdot 10^{-5}M$ (3) $8.4 \cdot 10^{-5}M$ (4) $1.1 \cdot 10^{-4}M$. Curves registered from —0.9V.

It is still better to use a $0.1M$ solution of a sodium salt of ethylendiamine-tetra-acetic acid of pH 6-8, with which well developed waves at concentrations as high as $5 \cdot 10^{-4}M$ are observed (Fig. 3). In this medium zinc and trivalent arsenic do not interfere.

SUMMARY

The nature of the two reduction waves of tetravalent germanium in ammonia-ammonium chloride buffer is described. Contrary to the statement of DASGUPTA AND NAIR[1] only the height of the first diffusion current should be used for analytical purposes. The second wave corresponds to a catalytic hydrogen evolution. The use of ethylenediaminetetra-acetic acid of pH 6-8 for the analysis of germanium is preferable[2].

RÉSUMÉ

La nature des deux vagues de réduction du germanium en solution tampon ammoniaque-chlorure d'ammonium est décrite. Contrairement aux dires de DASGUPTA ET NAIR[1], seule la mesure du premier courant de diffusion peut être utilisée pour l'analyse. La seconde vague correspond à une évolution catalytique de l'hydrogène. L'emploi d'acide éthylènediaminotétracétique au pH 6-8 pour le dosage du germanium est plus avantageux[2].

ZUSAMMENFASSUNG

Die Art der zwei Reduktionsstufen von tetravalentem Germanium in einem Ammonium-Ammoniumchloridpuffer wird beschrieben. Im Gegensatz zu den Feststellungen von DASGUPTA UND NAIR[1] soll nur die Höhe des ersten Diffusionsstromes zu analytischen Zwecken benutzt werden. Die zweite Stufe entspricht einer katalytischen Wasserstoffentwicklung. Die Verwendung von Äthylendiamintetraessigsäure bei pH 6-8 ist zur Analyse des Germaniums vorzuziehen[2].

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